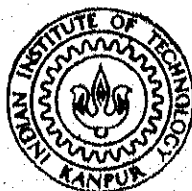


**SYNTHESIS AND REACTIVITY OF POLYSULFIDO COMPLEXES OF NICKEL  
PALLADIUM AND PLATINUM IN DIFFERENT OXIDATION STATES**

By  
**K. NAGENDRA UDPA**

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**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
APRIL 1985**

✓  
**SYNTHESIS AND REACTIVITY OF POLYSULFIDO COMPLEXES OF NICKEL  
PALLADIUM AND PLATINUM IN DIFFERENT OXIDATION STATES**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of

**DOCTOR OF PHILOSOPHY**

By  
**K. NAGENDRA UDPA**

to the

**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
APRIL 1985**

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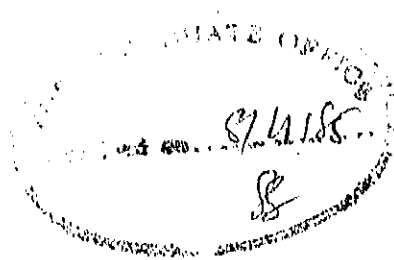
STATEMENT

I hereby declare that the matter embodied in this thesis "Synthesis and Reactivity of Polysulfido Complexes of Nickel, Palladium and Platinum in Different Oxidation States," is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Dr. S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

  
K.N. UDPA  
Candidate

Kanpur:  
April 1985.



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CERTIFICATE

Certified that the work "Synthesis and Reactivity of Polysulfido Complexes of Nickel, Palladium and Platinum in Different Oxidation States," presented in this thesis has been carried out by Mr. K. Nagendra Udpa under my supervision and the same has not been submitted elsewhere for a degree.

(S. SARKAR)  
Thesis Supervisor

Deptt. of Chemistry,  
IIT-Kanpur - 208016

Kanpur:

April 1985.

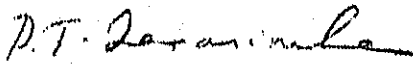
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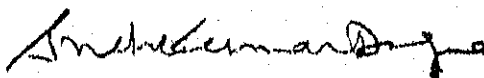
CERTIFICATE OF COURSE WORK

This is to certify that Mr. K. Nagendra Udpa has satisfactorily completed all the courses required for the Ph.D. degree program. The courses include:

Chm 501 Advanced Organic Chemistry I  
Chm 521 Chemical Binding  
Chm 524 Modern Physical Methods in Chemistry  
Chm 541 Advanced Inorganic Chemistry I  
Chm 800 General Seminar  
Chm 801 Graduate Seminar  
Chm 900 Post-Graduate Research

Mr. K. Nagendra Udpa was admitted to the candidacy of the Ph.D. degree in February 1981 after he successfully completed the written and oral qualifying examinations.

  
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(S.K. Dogra)  
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Many people have helped me by recording some of the spectra reported in this thesis and I extend my sincere thanks to all of them. I would like to make special mention of Dr. B. Folkesson, University of Lund, Sweden for the XPS measurements, Prof. H.D. Bist, I.I.T., Kanpur for the Raman spectrum, Dr. S.K. Dogra, I.I.T., Kanpur for the electronic spectra and Dr. P. Subramanian, Utah State University, U.S.A. for the cyclic voltammetric and differential pulse polarographic measurements.

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The single largest contribution in shaping me what I am today comes from the faith, hope and pride of my mother, brothers and sisters in me. It is their love that kept me going and I take this opportunity to offer my heartfelt thanks to them.

I.I.T., Kanpur  
April 1985.

K. NAGENDRA UDPA



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## SYNOPSIS

The thesis entitled "Synthesis and Reactivity of Polysulfido Complexes of Nickel, Palladium and Platinum in Different Oxidation States," has been divided into four chapters.

Chapter I describes a broad and general account of the versatility of  $S_x^{2-}$  ( $x = 2-9, \neq 7$ ) ions as ligands. Based on these, different synthetic strategies to generate these ligands coordinated to metal centers are outlined. Reactivity of coordinated polysulfide ring towards redox reactions and insertion reactions with the formation of newer heterocyclic rings are stressed upon.

Chapter II presents the scope of the present work, which stems from the fact that not much is known about the polysulfido complexes of nickel group of metals, though the first known compound containing polysulfide coordination to a metal center is of platinum(IV). Polysulfido compounds containing these metals would be important, as compounds of these metals are used as catalysts in many reactions. Another probable aspect of these compounds would be their unusual redox reactions, where reactions can take place either on the metal center or on the coordinated polysulfide group, leading thereby, the generation of hitherto unknown reactive species stabilized by coordination which might shed some light on our understanding of the sulfur cycle. In view of these, possible synthetic

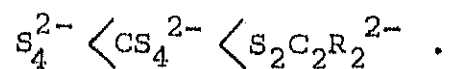
approaches for different sulfur containing heterocycles starting from polysulfido complexes have been outlined.

Chapter III which has been divided into seven parts describes the experimental procedures and the details involved in the present work. The first part 3.1 describes the methods of analysis and work-up manipulations of the newly prepared compounds. Part 3.2 describes the synthesis of complexes containing only polysulfide ligands, by reacting  $[M(CN)_4]^{2-}$  ( $M = Ni, Pd, Pt$ ) with polysulfide. Nickel gives only  $[Ni(S_4)_2]^{2-}$  anion whereas palladium gives  $[PdS_{11}]^{2-}$ ,  $[Pd(S_5)_3]^{2-}$  and  $[Pd(S_4)_2]^{2-}$  depending on the reaction conditions. Platinum gives only the well known  $[Pt(S_5)_3]^{2-}$ . Part 3.3 deals with the synthesis of polysulfido complexes containing other ligands also. Thus, by changing the reaction conditions anion of the type  $[(NC)_2Ni(S_5)]^{2-}$  has been stabilized. In addition to this several metal complexes of the general formula  $[M(L-L)(S_4)]$  (where  $M = Ni$  or  $Pd$ ;  $L-L$  = aromatic diimines) are isolated. Part 3.4 describes the reactions of polysulfido complexes with carbon disulfide and carbonyl sulfide. Complex anions of the type  $[M(CS_4)_2]^{2-}$  and  $[M(COS_3)_2]^{2-}$  ( $M = Ni$  or  $Pd$ ) are isolated, respectively. Starting from the neutral complexes, perthiocarbonato complexes of the general formula  $[Ni(L-L)(CS_4)]$  are isolated ( $L-L$  = aromatic diimines). Reactivity of  $CS_2$  with the complexes  $[M(S_5)_3]^{2-}$  ( $M = Pd$  or  $Pt$ ) has been investigated along with the capability of inserting  $CO_2$  in parallel to  $CS_2$  and  $COS$ . Part 3.5 describes

the reactions of polysulfido complexes containing  $S_4^{2-}$  and  $S_5^{2-}$  ligands with substituted acetylenes where the oxidation state of the metal varies from II to IV. With the bivalent complexes, compounds of the general formula  $[M(S_2C_2R_2)_2]^-$  ( $M = Ni$  or  $Pd$ ;  $R = COC_6H_5$  or  $COOCH_3$ ) are isolated. When the tetravalent complexes are used, compounds of the type  $[M(S_2C_2R_2)_3]^{2-}$  ( $M = Pd$  or  $Pt$ ) are isolated. Similarly  $[Pd(o\text{-phen})(S_4)]$  on treatment with  $R_2C_2$  gives  $[Pd(o\text{-phen})(S_2C_2R_2)]$ . Part 3.6 describes the synthesis of  $[Ni(L-L)(S_3O_2)]$  type of compounds in aerated medium ( $L-L =$  aromatic diimines). The last part 3.7 deals with the general discussion about the properties of these compounds and the synthetic strategies involved in their isolation. A possible role of some reactive intermediate like  $S_3O_2^{2-}$  relevant to sulfur cycle has been proposed by the ready formation of complexes described in 3.6.

Chapter IV describes the physico-chemical and structural investigations of the compounds described in the preceding chapter. The studies include electronic, infrared, Raman, X-ray photoelectron and electron spin resonance spectroscopy, cyclic voltammetry and magnetic susceptibility measurements. Emphasis has been made to characterize the complexes in conformation with the existing theories and with other related studies which appeared in the literature while our work was in progress. An attempt has been made to understand the relative strength of  $S_4^{2-}$ ,  $CS_4^{2-}$  and  $S_2C_2R_2^{2-}$  ( $R = COC_6H_5$ ,  $COOCH_3$ ) ligands in these

systems. The following order has been proposed:



In the  $[M(S_2C_2R_2)_2]^-$  ( $M = Ni$  or  $Pd$ ) complexes the highest occupied molecular orbital contains electron density of appreciable metal character suggesting a formal oxidation state of the metal ion in these complexes as +3.

## CHAPTER 1

### INTRODUCTION

The first compound containing coordinated polysulfide groups was reported in 1903 by Hofmann and Hochtlen [1]. However, most of the work in this fascinating field has been carried out only in the recent past. The coordination chemistry of the disulfide ion is reasonably well developed and an excellent review highlighting the various aspects of this chemistry has appeared in the literature recently [2]. The coordination chemistry of the higher polysulfide ions, however, is still in an embryonic state, although complexes of  $S_x^{2-}$  are known for upto  $x = 9$  (with the exception of  $x = 7$ ). The study of this chemistry is promising to be important considering the possible significance of such complexes in biochemistry and catalytic reactions of industrial importance such as the desulfurization of coal and oil. A brief review of this relatively new but rapidly growing area of chemistry has been made in this chapter.

### A. Syntheses

Polysulfido complexes have been prepared by a variety of methods. These preparative routes can be classified into following groups:

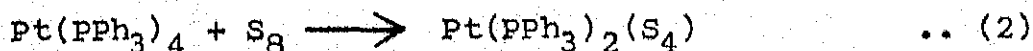
#### (1) Reaction of low-valent metal complexes with elemental sulfur

Addition of elemental sulfur to a coordinatively unsaturated, electron rich metal complex is a common route for the preparation of disulfido complexes. Addition of disulfide is accompanied by an oxidation of the metal center. For example, reaction (1):



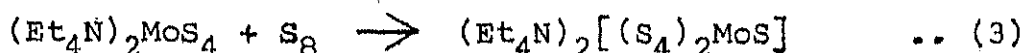
is very facile for metal atoms with  $d^8$  electronic configurations such as Ir(I), Rh(I), Ru(0) and Os(0) [3-9]. The additional ligands (L) are  $\pi$ -acceptor ligands such as CO and  $PPh_3$ . Coordination of the central metal atom, on addition of the disulfide, changes from square-planar to distorted octahedral.

Tetra- and pentasulfido complexes have also been prepared by this method [10-17]. An example of a tetrasulfido complex prepared by this route is [Eqn. (2)][10]:

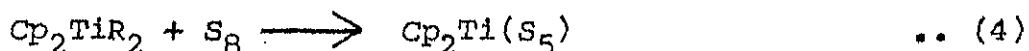


An example in which the metal center is reduced with the concomitant formation of a tetrasulfido complex is [Eqn. (3)][11]:

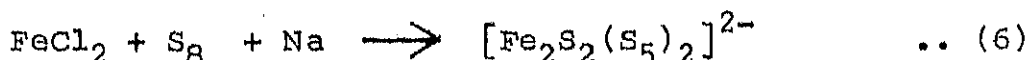
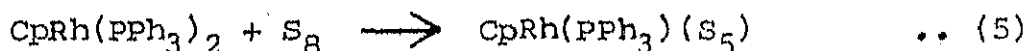




Equations (4-6) give representative examples of the pentasulfido complexes prepared by this method [12-14]:



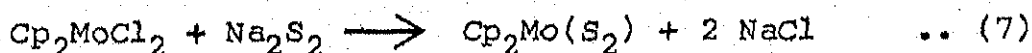
(R = CO, CH<sub>3</sub> or CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)



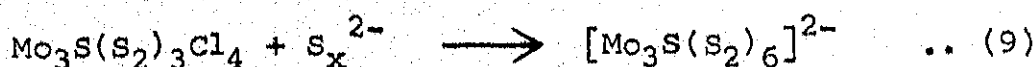
However, not all reactions of low-valent metal complexes with elemental sulfur proceed in such a straightforward manner. Many reactions produce mixtures of various metal sulfur complexes, often in low yield [18-27].

(ii) Reaction of metal salts or complexes with  $\text{S}_x^{2-}$

Substitution of  $\text{S}_2^{2-}$  for other ligands is a convenient method of introducing the disulfide ligand. For this purpose, either an alkali metal disulfide [Eqn. (7)][28]:



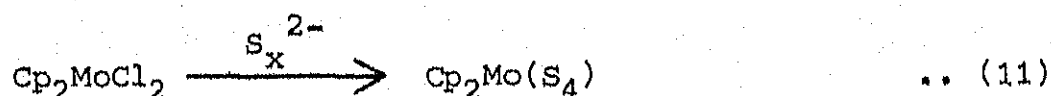
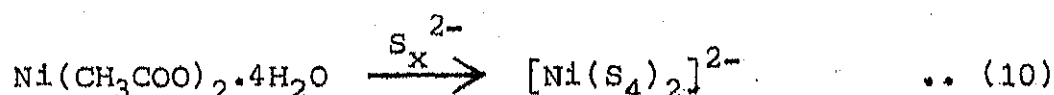
or a polysulfide solution [2] can be used [Eqns. (8) and (9)]:



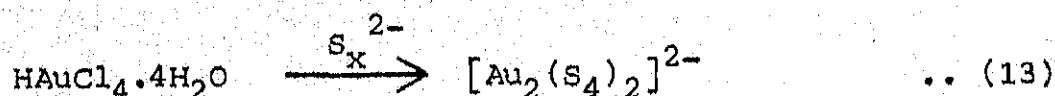
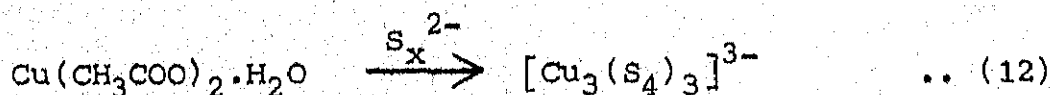
Aqueous polysulfide solutions are especially useful reagents for the synthesis of disulfido complexes [29-37]. The solutions are prepared by saturating an aqueous solution of ammonia after addition of sulfur with  $\text{H}_2\text{S}$ .

Reaction of  $\text{S}_x^{2-}$  with metal complexes is a versatile method for the synthesis of other polysulfido complexes as well. Thus, the reaction of  $(\text{Me}_5\text{C}_5)\text{MCl}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) with  $\text{Li}_2\text{S}_2$  and elemental sulfur in tetrahydrofuran under an inert atmosphere gives the novel trisulfido complex  $(\text{Me}_5\text{C}_5)_2\text{MS}_3$  [38]. Most likely the reaction proceeds through the formation of  $\text{S}_3^{2-}$  by the reaction of  $\text{S}_2^{2-}$  and elemental sulfur.

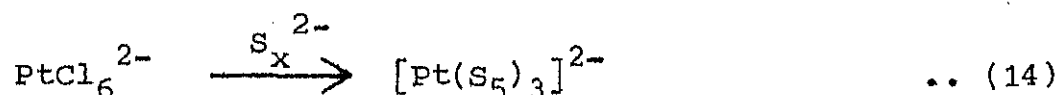
A number of tetrasulfido complexes have been prepared by the reaction of metal salts or complexes with  $\text{S}_x^{2-}$  in suitable solvent media [11, 39-45]. Representative examples are [Eqns. (10) and (11)] [41-43]:



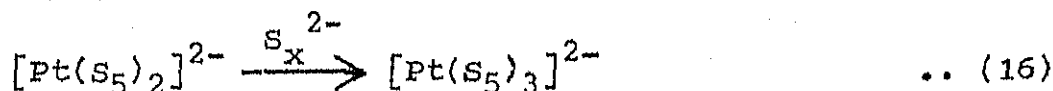
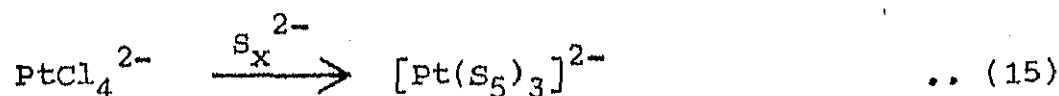
In some reactions the polysulfide acts as a reducing agent. For example, in Eqns. (12) and (13)  $\text{Cu}(\text{II})$  and  $\text{Au}(\text{III})$  are reduced to  $\text{Cu}(\text{I})$  and  $\text{Au}(\text{I})$ , respectively [39, 44]:



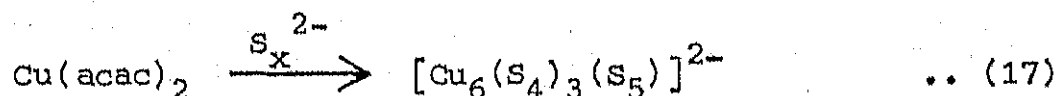
Reaction of metal salts or complexes with polysulfide ion  $S_x^{2-}$  is the most common method for the preparation of pentasulfido complexes [1,12,14,17,39,45-56]. An example is [Eqn. (14)][1]:



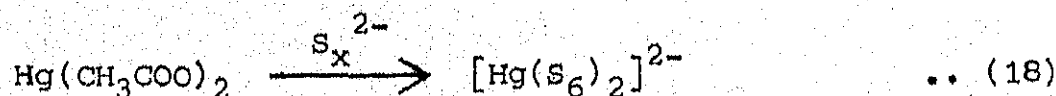
When the starting material is a compound of platinum(II) instead of platinum(IV), polysulfide oxidizes the metal center and the same platinum(IV) product is obtained [Eqns. (15) and (16)][56]:

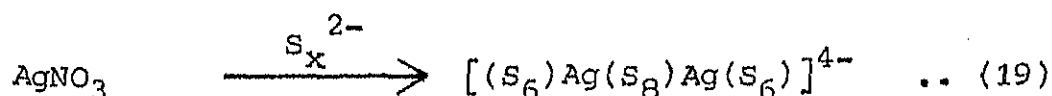


Examples are also known where the metal is reduced by the polysulfide [Eqn.(17)] [45]:



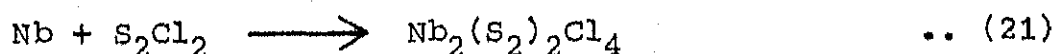
All the known hexasulfido [44,57-62], octasulfido [44-62] and nonasulfido [61,63] complexes have been prepared by the reaction of metal salts with polysulfide solution. Examples are [Eqns. (18 - 20)] [60,62,63]:



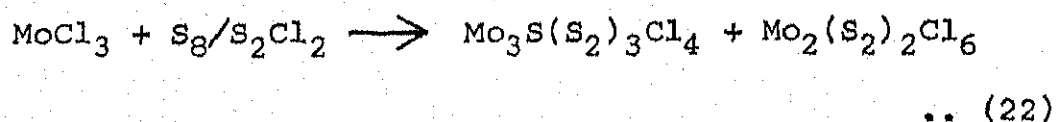


(iii) High temperature reaction of metals or metal halides with  $\text{S}_8$  and/or  $\text{S}_2\text{Cl}_2$

Several compounds with network structures which contain disulfide units can be prepared by high temperature (250-700°C) reactions. Examples are  $\text{Mo}_2(\text{S}_2)_2\text{Cl}_6$ ,  $\text{Mo}_3\text{S}(\text{S}_2)_3\text{Cl}_4$ ,  $\text{Nb}_2(\text{S}_2)_2\text{Cl}_4$  and  $\text{Na}_4\text{Re}_6\text{S}_{12}$  [64-71]. The sulfur containing reagent is  $\text{S}_2\text{Cl}_2$  or a mixture of  $\text{S}_8$  and  $\text{S}_2\text{Cl}_2$ . The metal is reacted in elemental form or as a low-valent chloride. For  $\text{S}_2\text{Cl}_2$ , the reaction involves the reduction of the formally positively charged  $\text{S}_2^{2+}$  unit [Eqn. (21)] [64]:



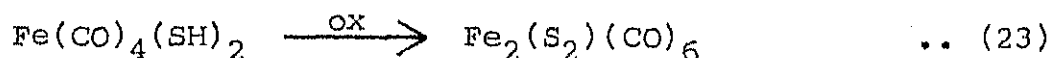
An example of a reaction of a metal halide with sulfur and  $\text{S}_2\text{Cl}_2$  is [Eqn. (22)] [68]:



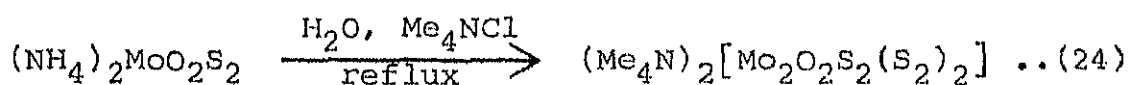
The conditions under which these  $\text{S}_2^{2-}$  containing cluster compounds are formed illustrate their high stability. However, till date no higher polysulfido complexes have been prepared by this method.

(iv) Oxidation of sulfur containing ligands

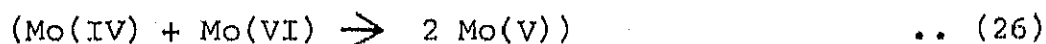
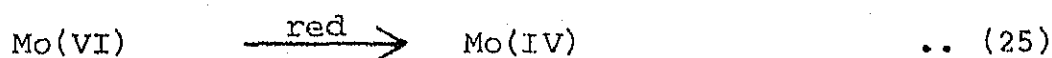
An interesting way of forming disulfide ligands is by the oxidation of two-SR ligands. One example is [Eqn. (23)] [72]:



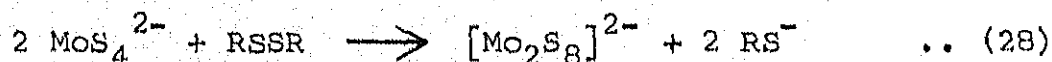
Intramolecular redox reactions within metal sulfido moieties are another important route for the synthesis of disulfido complexes. An example is the formation of  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{2-}$  from  $[\text{MoO}_2\text{S}_2]^{2-}$  [Eqn. (24)] [73,74]:



The following redox processes might be involved in this reaction:



Reaction of  $\text{MoS}_4^{2-}$  with organic disulfides is another example of the induced internal redox processes leading to the formation of a disulfido complex [Eqn. (28)] [75]:



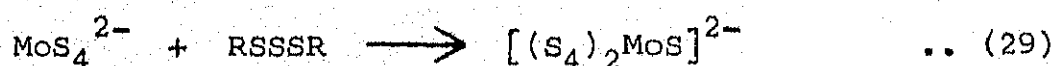
(R =  $\text{C}_6\text{H}_5$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ )

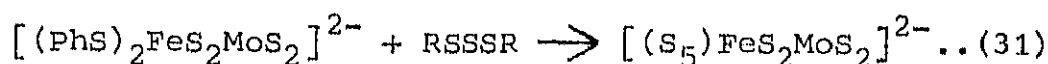
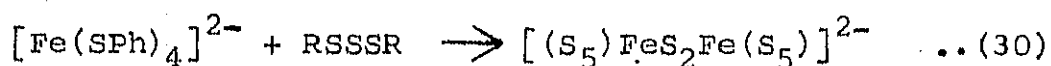
This stoichiometrically simple reaction involves a net two-electron oxidation with no overall gain or loss of sulfur atoms, i.e.,  $\text{Mo}_2\text{S}_8^{2-}$  is the dimer of the one-electron oxidation product of the hexavalent  $\text{MoS}_4^{2-}$ . Despite this net oxidation, the  $\text{Mo}_2\text{S}_8^{2-}$  product contains pentavalent molybdenum. Clearly, oxidation of the complex has caused the reduction of the metal.

Reaction (28) can be fruitfully represented as involving induced internal electron transfer from  $\text{S}^{2-}$  to  $\text{Mo(VI)}$ . A concomitant net two-electron oxidation of the ligand is required. The external oxidant, RSSR, takes up two electrons and each of the two Mo atoms takes up one electron. This requires a four-electron oxidation of the ligands, i.e., the conversion of four  $\text{S}^{2-}$  ligands to two  $\text{S}_2^{2-}$  ligands.

The induced internal redox concept can also be applied toward conceptual understanding of the remarkable reaction of  $\text{MoS}_4^{2-}$  with  $\text{S}_8$  to yield  $\text{MoS}_9^{2-}$  [Eqn. (3) vide supra] [11]. Here, formation of the  $\text{Mo(IV)}$  product is viewed as a result of internal redox from  $\text{S}^{2-}$  to  $\text{Mo(VI)}$  induced by the external oxidant  $\text{S}_8$ .

Organic trisulfides RSSSR react with metal complexes of sulfur containing ligands to form tetrasulfido [11,76] and pentasulfido [77-80] complexes. Examples are [Eqns. (29-31)] [76-78]:

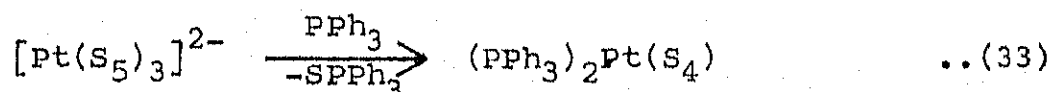
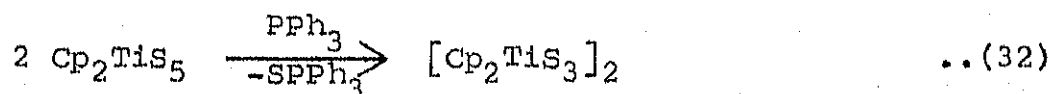




(v) Sulfur abstraction from metal polysulfido complexes

$[\text{Mo}_2\text{S}_{10}]^{2-}$ , a complex with terminal sulfido, bridging sulfido, disulfido and tetrasulfido groups is formed by the reaction of  $[\text{Mo}_2\text{S}_{12}]^{2-}$  with  $\text{PhSNa}$  [81]. The proposed mechanism involves the abstraction by the benzene thiolate of sulfur atoms from some of the disulfido groups of the initial complex, with some subsequent insertion of two sulfur atoms into one of the remaining terminal disulfido groups. However, why the particular complex should be formed is not clear.

Phosphines react with pentasulfido complexes forming tri- [82] and tetrasulfido [40,83,84] complexes. Examples are [Eqns. (32) and (33)] [82,83]:



Abstraction of sulfur from  $[\text{Pt}(\text{S}_5)_3]^{2-}$  by stoichiometric amounts of nucleophile such as  $\text{CN}^-$  leads to the formation of  $[\text{Pt}(\text{S}_5)_2]^{2-}$  [56,85]. The sulfur abstraction is accompanied by a concomitant reduction of  $\text{Pt(IV)}$  to  $\text{Pt(II)}$ .

(vi) Reactions with other sulfur containing reagents

The formation of disulfido complexes by other sulfur containing reagents such as  $\text{H}_2\text{S}$  [86-88],  $\text{P}_4\text{S}_{10}$  [21],  $\text{COS}$  [86,89,90],  $\text{R}_2\text{S}_x$  [86,91-93] and  $\text{Na}_2\text{SO}_3$  [20] have also been reported. Here, however, the mechanisms of these reactions are not well understood.

The formation of polysulfido complexes is very sensitive to the reaction conditions such as the ratio of reagents, the solvent employed and the nature of the counterions present in solution. Reaction of cupric acetate with polysulfide provides an excellent example of this. In purely ethanolic medium and in the presence of  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{I}$  the trinuclear hexasulfido complex  $[\text{Cu}_3(\text{S}_6)_3]^{3-}$  is obtained [59]. Addition of ethanolic ammonium polysulfide to a solution of cupric acetate and  $\text{PPh}_4\text{Br}$  in acetonitrile gives an orange-red solution which on keeping precipitates discrete copper-sulfur aggregates  $[\text{Cu}_4\text{S}_x]^{2-}$  ( $x = 13-15$ ) [39]. In purely acetonitrile medium and with a polysulfide solution of lesser sulfur content,  $[\text{Cu}_3(\text{S}_4)_3]^{3-}$  is obtained [44]. Under similar conditions but with a polysulfide solution containing large amounts of sulfur, the sulfur rich  $[(\text{S}_6)\text{Cu}(\text{S}_8)\text{Cu}(\text{S}_6)]^{4-}$  is obtained [44]. When the starting compound is  $\text{Cu}(\text{acac})_2$  and the reaction is carried out in ethanol-dimethylformamide medium  $[\text{Cu}_6(\text{S}_4)_3(\text{S}_5)]^{2-}$  is formed [45]. This compound can also be prepared by the reaction of copper(I) thiolate with elemental sulfur [17].



Molybdenum is another metal which forms many polysulfido complexes. Here also the products obtained are very sensitive to the reaction conditions. The reaction of  $(\text{Et}_4\text{N})_2\text{MoS}_4$  with  $(\text{C}_7\text{H}_7)\text{SSS}(\text{C}_7\text{H}_7)$  or elemental sulfur in  $\text{CH}_3\text{CN}$ , either under a dinitrogen atmosphere or in the air, proceeds readily at ambient temperature, and  $(\text{Et}_4\text{N})_2[(\text{S}_4)_2\text{MoS}]$  is formed and can be isolated in excellent yields [11]. Attempts to exchange the  $\text{Et}_4\text{N}^+$  cations in this complex with  $\text{Ph}_4\text{P}^+$  in DMF solution were unsuccessful. Apparently, a dissociation and rearrangement of the sulfide ligands occurs in DMF solution following the addition of  $\text{Ph}_4\text{PCl}$ . The only product that can be isolated in crystalline form is a mixture of the  $(\text{Ph}_4\text{P})_2[\text{Mo}_2\text{S}_{10}]$  and  $(\text{Ph}_4\text{P})_2[\text{Mo}_2\text{S}_{12}]$  complexes. These complexes are also obtained when  $(\text{Ph}_4\text{P})_2\text{MoS}_4$  is treated with either elemental sulfur or  $(\text{C}_7\text{H}_7)\text{SSS}(\text{C}_7\text{H}_7)$  in DMF solution at room temperature. When DMF solutions of  $(\text{Et}_4\text{N})_2[(\text{S}_4)_2\text{MoS}]$  are heated, in the presence of traces of water, hydrolysis takes place and the yellow-green  $(\text{Et}_4\text{N})_2[(\text{S}_4)_2\text{MoO}]$  complex can be isolated in fair yields [11].

In the reaction of the aqueous polysulfide solution with  $\text{MoO}_4^{2-}$  the Mo(VI) is reduced and the products obtained depend upon the sulfur content of the polysulfide solutions. When dilute polysulfide solutions are used, at  $90^\circ\text{C}$  the Mo(IV) cluster compound  $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6] \cdot n\text{H}_2\text{O}$  ( $n = 0-2$ ) is formed. From the corresponding filtrate at lower temperatures, the Mo(V) complex  $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6] \cdot 2\text{H}_2\text{O}$  is obtained [36]. Addition of  $\text{NH}_2\text{OH}$  to the same solution gives the tetranuclear

$[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$  [37]. When a polysulfide solution containing large excess of sulfur is used, then a nearly quantitative yield of  $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6] \cdot \text{nH}_2\text{O}$  is obtained [37]. But, heating this solution to  $70^\circ\text{C}$  for a few minutes gives  $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6] \cdot 2\text{H}_2\text{O}$  [2]. Heating a solution of  $(\text{PPh}_4)_2\text{MoS}_4$  in DMF with methanolic polysulfide gives  $(\text{PPh}_4)_2[\text{Mo}_2(\text{S}_2)_6]$  [2].

Addition of  $\text{Ph}_4\text{PCl}$  to  $\text{CH}_3\text{CN}$  solutions of  $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]$  and upon standing, the  $[\text{Mo}_2\text{S}_{10}]^{2-}$  and  $[\text{Mo}_2\text{S}_{12}]^{2-}$  (structural isomer of  $[\text{Mo}_2(\text{S}_2)_6]^{2-}$ ) complex anions form and cocrystallize as  $\text{Ph}_4\text{P}^+$  salts [11]. A survey of the reaction of  $\text{MoS}_4^{2-}$  with active sulfur reagents and a consideration of the various thiomolybdate products obtained reveal a very complex system of equilibria. In such a system the individual species are interrelated either by the gain or loss of sulfur fragments or by facile molecular rearrangements. A tentative scheme proposed by Coucouvanis *et al.*, that attempts to correlate the various  $\text{MoS}_4^{2-}$  derived thioanions, is shown in Fig. 1.1 [11]. The formation of  $(\text{Mo}_2\text{S}_7)^{2-}$  (A, Fig. 1.1) during the acidifications of aqueous solutions of  $\text{MoS}_4^{2-}$  has been proposed previously on the basis of pH and conductometric titrations [94]. The same anion has been suggested as a bridging unit in the  $[\text{Fe}(\text{salen})]_2^{2-}(\text{Mo}_2\text{S}_7)$  complex [95]. More recently the  $(\text{Mo}_2\text{S}_7)^{2-}$  intermediate has been suggested to precede the formation of the  $[(\text{MoS}_4)_2\text{MoS}]^{2-}$  complex (B, Fig. 1.1) from  $\text{MoS}_4^{2-}$  in DMF solution. In a tentative proposed mechanism [96], internal electron transfer within the  $(\text{Mo}_2\text{S}_7)^{2-}$  will yield the



$[\text{Mo}^{\text{VI}}\text{S}_4\text{Mo}^{\text{IV}}\text{S}(\text{S}_2)]^{2-}$  anion, in which displacement of  $\text{S}_2^{2-}$  by  $\text{MoS}_4^{2-}$  will give the  $[(\text{MoS}_4)_2\text{MoS}]^{2-}$  complex (B, Fig. 1.1). Alternatively, this complex and the  $[(\text{S}_2)\text{MoS}(\text{S}_2)]^{2-}$  anion could be obtained also by the disproportionation of the  $[\text{Mo}^{\text{VI}}\text{S}_4\text{Mo}^{\text{IV}}\text{S}(\text{S}_2)]^{2-}$  anion.

In reaction where either active sulfur ( $\text{S}_x^0$ ,  $x = 2$ ) or polysulfide anions ( $\text{S}_x^{2-}$ ,  $x = 4$ ) are available, the  $[(\text{MoS}_4)\text{MoS}(\text{S}_2)]^{2-}$  intermediate could undergo either addition of  $\text{S}_2^0$  or displacement of  $\text{S}_2^{2-}$  by  $\text{S}_4^{2-}$  to yield the  $[(\text{MoS}_4)\text{MoS}(\text{S}_4)]^{2-}$  complex, which could exist in a disproportionation equilibrium with the  $[(\text{MoS}_4)_2\text{MoS}]^{2-}$  and  $[(\text{S}_4)_2\text{MoS}]^{2-}$  complexes.

In a series of sulfur transfer equilibria, and with the possible involvement of solvent ligation, either the  $[(\text{S}_4)_2\text{MoS}]^{2-}$  anion or the (as yet unknown)  $\text{MoS}_5^{2-}$  anion could give the  $[\text{Mo}_2\text{S}_{12}]^{2-}$ ,  $[\text{Mo}_2\text{S}_{10}]^{2-}$  and  $[\text{Mo}_2\text{S}_8]^{2-}$  thioanions (D-F, Fig. 1.1). All these three anions have been isolated and characterized by X-ray crystal structure determination [11,75].

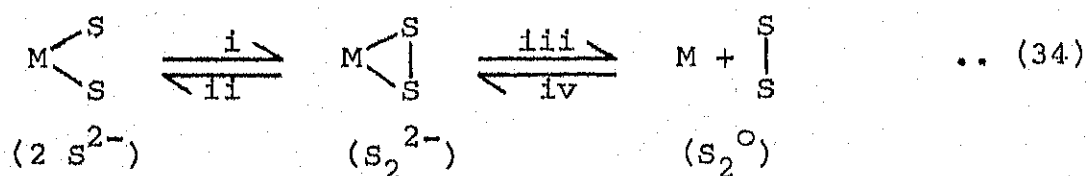
At present the  $[(\text{S}_2)\text{MoS}(\text{S}_2)]^{2-}$  and  $[(\text{S}_2)\text{MoS}(\text{S}_4)]^{2-}$  anions have not been isolated or detected, and their introduction in the general scheme (Fig. 1.1) is only speculative. However, their possible existence is justified on the basis of the demonstrated ability of the  $\text{S}_2^{2-}$  and  $\text{S}_4^{2-}$  anions to serve as ligands for either the  $(\text{Mo}=\text{S})^{2+}$  or  $(\text{Mo}=\text{S})^{3+}$  units. A consideration of the synthetic aspects of thiomolybdate chemistry shows that the nature of the counter ion present in solution and

other reaction conditions are very important in the isolation of specific complexes from equilibrium mixtures. It appears that the serendipitous choice of counter ion and reaction conditions may well be very important for the isolation of such proposed species as the  $[(S_2)MoS(S_2)]^{2-}$ ,  $[S_2MoS(S_4)]^{2-}$ , and  $[(MoS_4)MoS(S_4)]^{2-}$  anions and also such other species which are as yet unthought of.

## B. Reactions

### (i) Electron transfer and intramolecular redox reactions

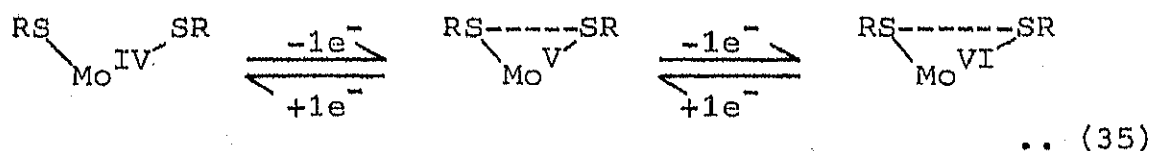
The redox behavior of polysulfido complexes particularly that of disulfido complexes is of interest because it can probably provide a foundation for understanding the course of reactions in enzymes and catalysts (especially desulfurization catalysts). Oxidation and reduction reactions related to disulfide ligands can be summarized by reaction scheme (34):



Examples of reaction (i) of (34) are provided by the oxidations of =S and -SR groups described in the previous section [72,73, 97-99]. Reaction (ii) of (34) involves reduction of the S-S bond to form two sulfido groups [100,101].

The reduction of a disulfido complex can follow reaction paths other than (ii). For example, electrochemical reduction of  $[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$  results in dissociation of  $\text{S}_2^-$  from the complex [102].

Reaction sequence (35) proposed by Stiefel et al. [103] for molybdenum enzymes is directly related to reactions (i) and (ii) of (34). In this context it is interesting to note that organic disulfides as well as disulfido complexes undergo reactions with low-valent metal complexes to form complexes with two sulfido ligands [100,101] or trinuclear sulfido-bridged complexes [100,104-106]:



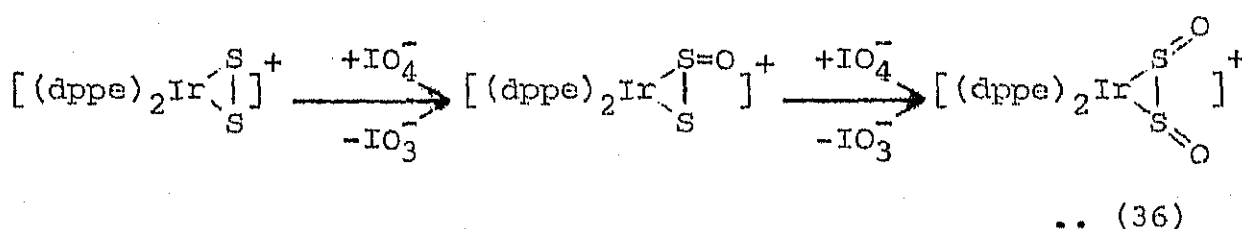
Reaction sequences (i) and (ii) of (34) and the proposal of Stiefel et al. [Eqn. (35)] also give new importance to the methylation reactions of  $\text{S}_2^{2-}$  complexes in which the S-S bond remains intact [4,7,88,107]. An example of reaction (iii) of (34) is the thermal decomposition of  $\text{Cs}_2[\text{Mo}_2(\text{S}_2)_6] \cdot n\text{H}_2\text{O}$  to give  $\text{S}_2$  as the main gaseous product [2]. Examples of reaction (iv) of (34) are provided by the synthesis of disulfido complexes from reactions employing elemental sulfur (vide supra).

The electrochemical one-electron oxidation of  $\text{Cp}_2\text{Fe}_2(\text{S}_2)-(\text{SEt})_2$  results in the formation of a metal-metal bond rather

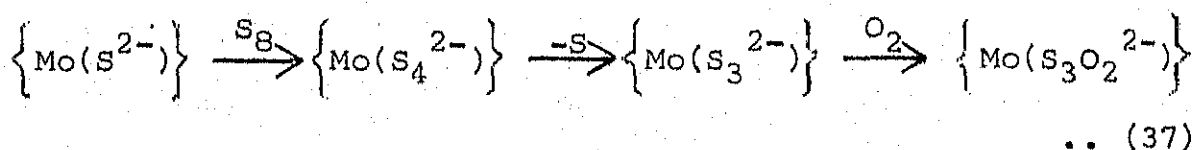
than in extrusion of sulfur [reaction (iii) of (34)] or the coupling of two-SET groups [sequence (35)]. The chemical two-electron oxidation in acetonitrile results in the elimination of disulfide and the formation of  $[\text{Cp}_2\text{Fe}_2(\text{MeCN})_2(\text{SEt})_2]^{2+}$  [91, 108, 109].

(ii) Oxidation of the ligand by external agents

In  $[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$  the disulfide ligand can be oxidized stepwise on the metal to form  $\text{S}_2\text{O}^{2-}$  and  $\text{S}_2\text{O}_2^{2-}$  complexes [Eqn. (36)] [110, 111]:



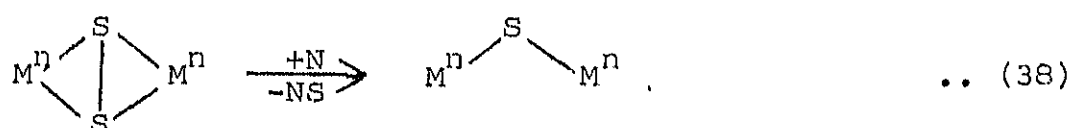
The synthesis of the complex containing  $\text{S}_3\text{O}_2^{2-}$  ligand  $[(\text{S}_2)\text{OMoS}_2\text{MoO}(\text{S}_3\text{O}_2)]^{2-}$  from  $[\text{MoOS}_3]^{2-}$  and elemental sulfur in presence of air probably proceeds according to Scheme (37) [112] involving the oxidation of the coordinated  $\text{S}_3^{2-}$  ligand:



However, refluxing  $[(\text{S}_4)_2\text{MoS}]^{2-}$  in DMF containing trace amounts of water leads to the formation of  $[(\text{S}_4)_2\text{MoO}]^{2-}$  [11].

(iii) Reaction with nucleophiles (abstraction of  $S^0$ )

A characteristic reaction of the polysulfido complexes<sup>†</sup> is the abstraction of sulfur atoms by nucleophiles (N) such as  $PPh_3$ ,  $SO_3^{2-}$ ,  $SR^-$ ,  $CN^-$  and  $OH^-$ . In disulfido complexes the sulfur atom abstraction takes place according to reaction (38) [90,107,113-116]:



The reaction involves loss of a neutral sulfur atom from the complex with no change in the formal oxidation state of the metal atoms. This reaction occurs especially in disulfido complexes in which there is substantial transfer of electron density from the ligand to the metal so that the population of the ligand  $\pi^*$  level is decreased [90,107,113].

In this regard the reaction of  $[Mo_3S(S_2)_6]^{2-}$  with  $CN^-$  is particularly interesting as a possible model for the inhibition of xanthine oxidase by  $CN^-$  with the concomitant formation of  $SCN^-$  [117,118]. The bridging disulfide ligands are converted to bridging sulfido ligands and the terminal  $S_2^{2-}$  groups are replaced by  $CN^-$  ligands [113].

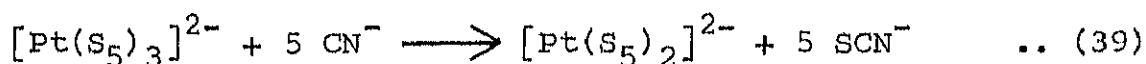
Reactions of  $[Mo_2(S_2)_6]^{2-}$  with nucleophiles also convert the bridging disulfide ligands to bridging sulfido ligands.

With weak nucleophiles the units  $[Mo \begin{array}{c} O \\ || \\ \diagdown \quad \diagup \\ S \quad S \\ \diagup \quad \diagdown \\ O \end{array} Mo]^{2+}$  [115] and

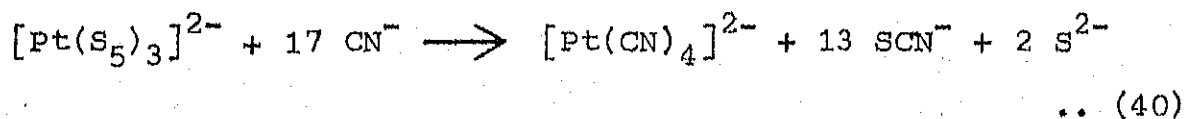


$\left[ \text{Mo} \begin{array}{c} \text{S} \\ \parallel \\ \text{S} \end{array} \text{S} \begin{array}{c} \text{S} \\ \parallel \\ \text{S} \end{array} \text{Mo} \right]^{2+}$  [81,114,116] are formed. With strong nucleophile  $\text{CN}^-$  the final product is  $\left[ (\text{CN})_4\text{Mo} \begin{array}{c} \text{S} \\ \parallel \\ \text{S} \end{array} \text{Mo}(\text{CN})_4 \right]^{6-}$  [115] and the molybdenum atoms have been reduced from oxidation state V to III. Clearly  $[\text{Mo}_2(\text{S}_2)_6]^{2-}$  is a useful starting material for the generation of other molybdenum-sulfur compounds.

Reaction of  $[\text{Pt}(\text{S}_5)_3]^{2-}$  with nucleophiles sulfite, arsenite, sulfide, hydroxide, cyanide and  $\text{PR}_3$  in stoichiometric amounts leads to the loss of one  $\text{S}_5^{2-}$  ligand and formation of  $[\text{Pt}(\text{S}_5)_2]^{2-}$  [Eqn. (39)] [56,85]. The desulfurization reaction



is accompanied by a concomitant reduction of Pt(IV) to Pt(II). With excess of nucleophile all the sulfur atoms are removed from the platinum [Eqn. (40)]:

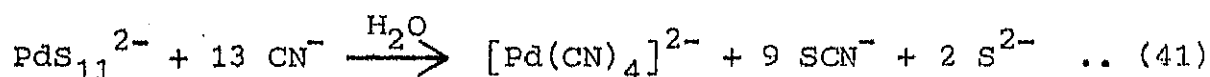


Attempts to synthesize  $[\text{Pt}(\text{S}_5)_2]^{2-}$  from polysulfide and a platinum(II) salt result in the formation of  $[\text{Pt}(\text{S}_5)_3]^{2-}$  where polysulfide acts as the oxidizing agent (vide supra). In view of this ready oxidation of Pt(II) to Pt(IV) in polysulfide medium, the reduction which accompanies the nucleophilic

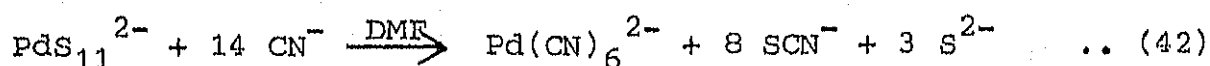
degradation of the first ring in  $[\text{Pt}(\text{S}_5)_3]^{2-}$  is quite surprising. However, an unusual type of electron transfer by coordinated sulfide or polysulfide ion, is proposed for the reduction of Pt(IV) [56].

Reaction of pentasulfido complexes with excess of phosphines, however, result in the formation of lower polysulfido complexes such as  $\text{Pt}(\text{PPh}_3)_2(\text{S}_4)$  and  $[\text{Cp}_2\text{TiS}_3]_2$  (vide supra) [40,82-86].

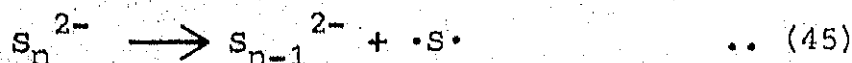
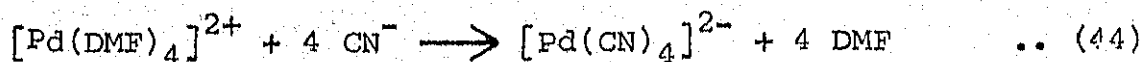
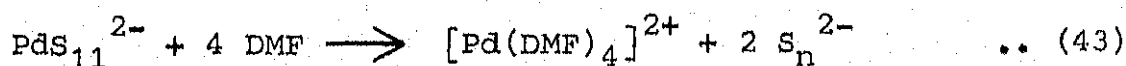
Reaction of  $\text{PdS}_{11}^{2-}$  with  $\text{CN}^-$  leads to complete desulfurization [Eqn. (41)] [58]:



In DMF medium, however, a very interesting reaction occurs where Pd(II) is oxidized to Pd(IV), [Eqn.(42)] [58]:

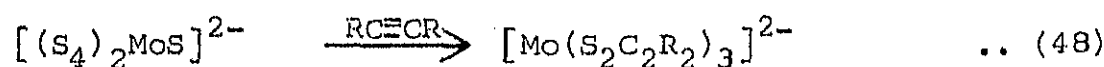
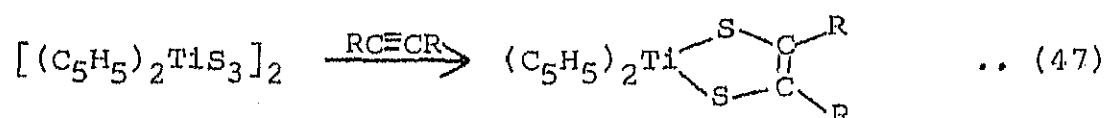


The sulfur radical anion present in the DMF solutions of polysulfide is proposed to be the oxidant. The suggested reaction scheme is as follows:



(iv) Reaction with substituted acetylenes

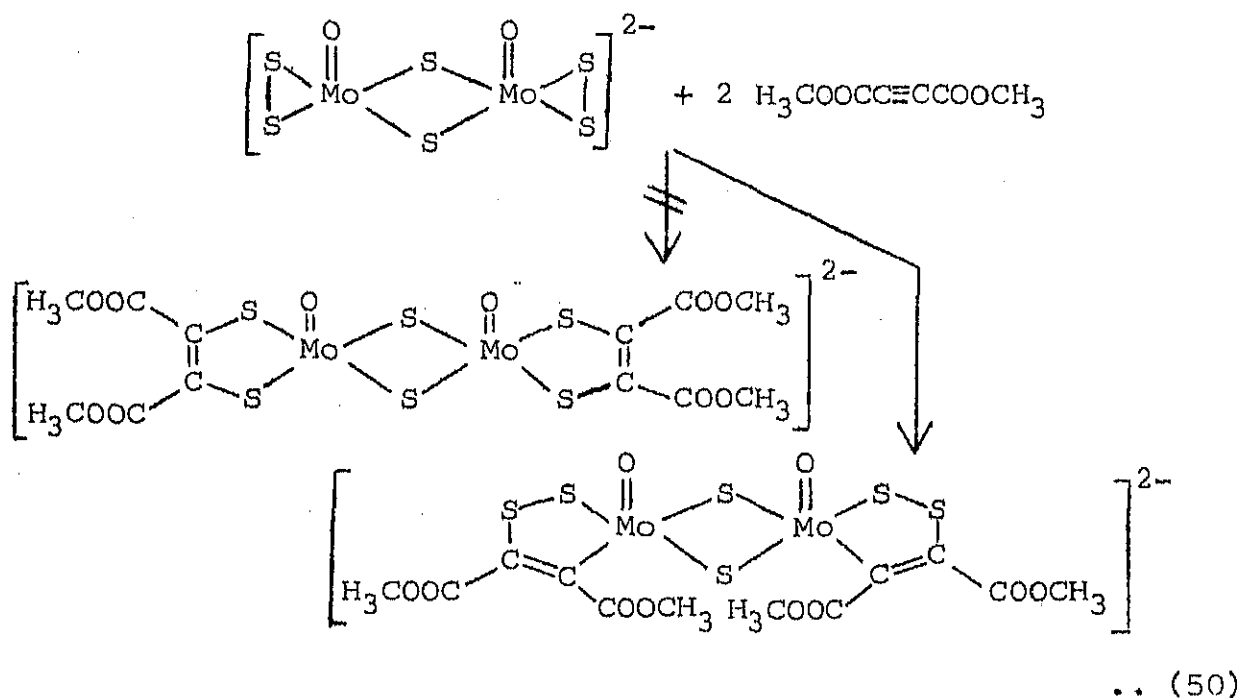
Substituted acetylenes  $RC\equiv CR$  ( $R = CO_2CH_3, CF_3$ ) react with polysulfido complexes forming 1,2-dithiolate complexes. Representative examples are given in equations (47-49) [82, 119-123]:



At present the mechanisms of these reactions are not understood. Probably the presence of electron withdrawing carboxylate group in the molecule renders the acetylenic carbon atom susceptible to nucleophilic attack by the sulfur lone pairs of the  $S_x^{2-}$  ligand. Apparently two sulfur atoms from the  $S_x^{2-}$  ligand become available for the formation of the 1,2-dithiolate moiety. The fate of the remaining sulfur atoms in the  $S_x^{2-}$  ligand remains to be established, however, it is quite likely that they eventually form elemental sulfur.

The reaction of  $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$  with dimethylacetylenedicarboxylate, however, does not give the expected 1,2-dithiolate complex, but, instead the acetylenes insert into Mo-S

bonds of the terminal disulfides to form five-membered metallacyclopent-2,3-dithiacyclopent-4-ene rings [Scheme (50)] [124]:

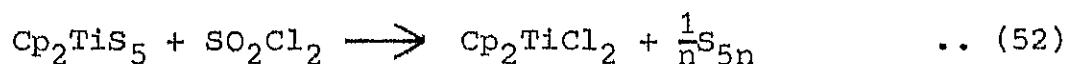
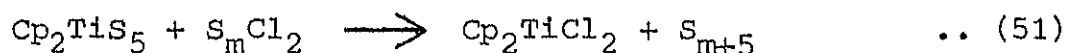


The reason why the insertion takes place into Mo-S bonds rather than into S-S bonds is not clear.

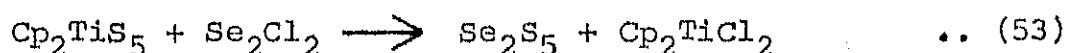
#### (v) Other reactions

The thermal decomposition of  $\text{Cs}_2[\text{Mo}_2(\text{S}_2)_6] \cdot n\text{H}_2\text{O}$  at rather low temperatures (100–200°C) gives  $\text{S}_2$  molecule as the main gaseous product which results from a reductive elimination process [2]. The solid residue contains  $\text{Cs}_2[\text{Mo}_3\text{S}(\text{S}_2)_6]$  at 270°C. The thermal decomposition of  $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6] \cdot n\text{H}_2\text{O}$  at 270°C produces one mole of  $\text{NH}_3$  and half a mole of  $\text{H}_2\text{S}$  per mole of the trinuclear complex [125].

Various sulfur homocycles can be conveniently prepared by the reaction of  $\text{Cp}_2\text{TiS}_5$  with chlorosulfanes or  $\text{SO}_2\text{Cl}_2$  [Eqns. (51) and (52)] [126-128]:

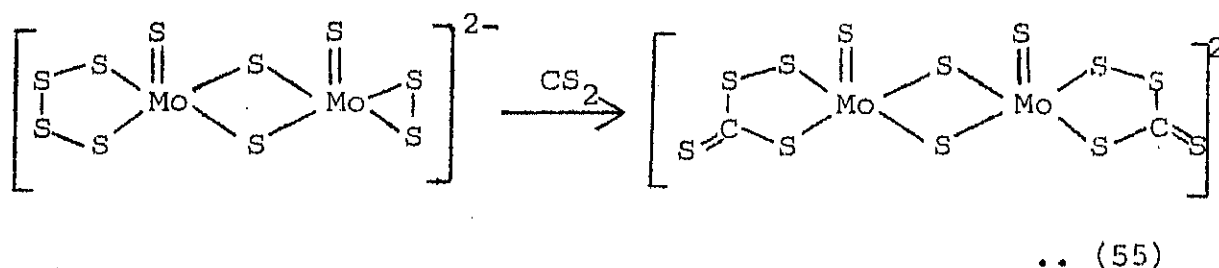
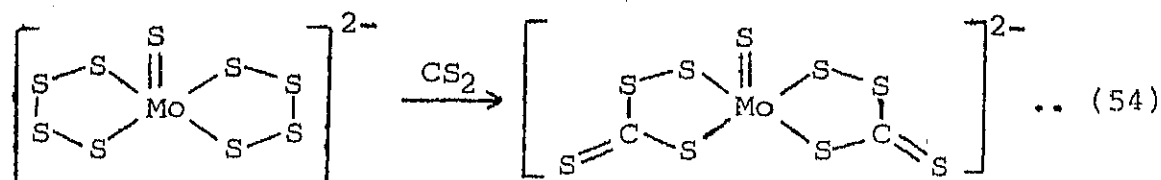


In a similar manner the reaction with  $\text{Se}_2\text{Cl}_2$  produces  $\text{Se}_2\text{S}_5$  [Eqn. (53)] [129]:



Methyl iodide reacts readily with  $[\text{Pt}(\text{S}_4)(\text{PPh}_3)_2]$  and  $[\text{Pt}(\text{S}_4)(\text{dppe})]$  in either THF or alcohols [130]. However, the nature of the products is very sensitive to the molar ratio of the reactants and the reaction times. If long reaction times are used with excess of methyl iodide, then the major product is  $[\text{PtI}_2(\text{PPh}_3)_2]$  or  $[\text{PtI}_2(\text{dppe})]$ . An intermediate of the formula  $[\text{Pt}(\text{S}_4(\text{CH}_3)_2)(\text{PPh}_3)_2]\text{I}_2$  can also be isolated when a molar ratio of 1:2 is used.

The coordinated  $\text{S}_4^{2-}$  ligand in  $[(\text{S}_4)_2\text{MoS}]^{2-}$  and  $\text{S}_4^{2-}$  and  $\text{S}_2^{2-}$  ligands in  $[\text{Mo}_2\text{S}_{10}]^{2-}$  react with  $\text{CS}_2$  forming perthio-carbonate ligands [Eqns. (54) and (55)] [131]:



The formation of the  $\text{CS}_4^{2-}$  ligands may proceed via electrophilic attack by  $\text{CS}_2$  on the coordinated  $\text{S}_4^{2-}$  ligands with subsequent rearrangement and elimination of  $\text{S}_2$ . Another mechanism for this reaction could be one in which  $\text{S}_2$  dissociation from the coordinated  $\text{S}_4^{2-}$  ligands allows for the formation of  $\text{Mo} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array}$  units. From such units the  $\text{Mo-CS}_4$  units may be obtained from  $\text{CS}_2$  by electrophilic attack on one of the two sulfur atoms of the disulfide ligand, by insertion into the  $\text{Mo-S}$  bond and rearrangement, or by a cycloaddition reaction.

### C. Physical Measurements

#### (i) Vibrational spectra

In polysulfido complexes the  $\nu(\text{S-S})$  frequencies range from ca. 400 to 600  $\text{cm}^{-1}$ . Comparison of the  $\nu(\text{S-S})$  values for the discrete diatomic sulfur species  $\text{S}_2$  (725  $\text{cm}^{-1}$ ) [2],  $\text{S}_2^-$  (589  $\text{cm}^{-1}$ ) [132-133] and  $\text{S}_2^{2-}$  (446  $\text{cm}^{-1}$ ) [134] leads to

the conclusion that in disulfido complexes the approximate charge distribution is somewhere between that for  $S_2^-$  and that for  $S_2^{2-}$ . However, in this comparison the strong coupling of the  $\nu(S-S)$  vibration with the  $\nu(M-S)$  vibrations which lead to higher  $\nu(S-S)$  must also be considered. The intensities and the band position depend upon the structural type of the polysulfido complex (vide infra).

The  $\nu(M-S)$  bands are generally observed in the range 250 to 420  $cm^{-1}$ . Both  $\nu(S-S)$  and  $\nu(M-S)$  for some of the polysulfido complexes are listed in Table 1.1. Vibration spectral data for many other compounds have also been reported [10, 39-44, 53, 60-63] but no band assignments have been made.

Approximate normal coordinate analysis has been carried out for many disulfido complexes. Comparison of the force constants of the S-S bond with those of  $S_2^{n-}$  ( $n = 0-2$ ) species confirms the conclusion drawn from the S-S frequencies, that is, the S-S bond strength in disulfido complexes lies between that for  $S_2^-$  (bond order = 1.5) and that for  $S_2^{2-}$  (bond order = 1.0) [135-136].

#### (ii) X-ray photoelectron spectra

The X-ray photoelectron spectra of several disulfido complexes [2, 134] and of  $(NH_4)_2[Pt(S_5)_3]$  [139] have been reported. The  $S_{2p}$  binding energies (Table 1.2) lie between 162.9 and 164.8 eV indicating that the sulfur atoms are

Table 1.1 Frequencies for  $\nu(\text{S-S})$  and  $\nu(\text{M-S})$  vibrations of polysulfido complexes

Complex	$\nu(\text{S-S})^a (\text{cm}^{-1})$	$\nu(\text{M-S})^a (\text{cm}^{-1})$	Ref.
$[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$	528	369, 350	3
$\text{MoO}(\text{S}_2)(\text{dtc})_2$	556	374, 350	87
$\text{Cp}_2\text{Mo}(\text{S}_2)$	530	386, 351	28
$\text{Nb}_2(\text{S}_2)_2\text{Cl}_4$	588	377, 362, 336 <sup>b</sup> , 323, 317 <sup>b</sup>	135
$[\text{Zr}_2\text{S}_2(\text{S}_2)_2\text{Cl}_4]_n$	529	365, 326 <sup>b</sup>	136
$\text{Fe}_2(\text{S}_2)(\text{CO})_6$	555	332, 310	137, 138
$[\text{Ni}(\text{S}_4)_2]^{2-}$	480, 480 <sup>b</sup> , 430, 375	293 <sup>b</sup> , 280	43
$[\text{Au}_2(\text{S}_4)_2]^{2-}$	488 <sup>b</sup> , 475 <sup>b</sup> , 446 <sup>b</sup>	-	39
$\text{Pt}(\text{S}_4)(\text{PPh}_3)_2$	-	315, 312, 310	130
$\text{Pt}(\text{S}_4)(\text{dppe})$	-	326, 315	130
$[\text{Pt}(\text{S}_5)_3]^{2-}$	490, 450	294	56
$[\text{Fe}_2\text{S}_2(\text{S}_5)_2]^{2-}$	474	414, 338, 315	14
$[\text{Mo}(\text{NO})_2(\text{S}_2)_3^-$ $(\text{S}_5)(\text{OH})]^{3-}$	521, 474, 425	341, 315	54
$[(\text{S}_6)\text{Ag}(\text{S}_8)-$ $\text{Ag}(\text{S}_6)]^{4-}$	490 <sup>b</sup> , 454 <sup>b</sup> , 442 <sup>b</sup> , 411 <sup>b</sup> , 394 <sup>b</sup>	-	62
$[\text{Cu}_3(\text{S}_6)_3]^{3-}$	453	253	59

<sup>a</sup>IR bands unless otherwise stated;

<sup>b</sup>Raman bands.



generally more negatively charged than in neutral sulfur ( $S_{2p}$  binding energy for  $S_8$  is 164.2 eV) [140]. The corresponding binding energy for sulfur in complexes with reduced sulfur containing ligands such as  $S^{2-}$ ,  $-\overset{|}{\underset{|}{C}}-S^-$ ,  $-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-$  or  $>C=S$  are in the range 161.5 - 163.5 eV [141].  $Na_2S$  has a binding energy of 162.0 eV [140] and thiometallates have binding energies of 162.2 - 163.4 eV [142]. Thus, the  $S_{2p}$  binding energy for disulfido complexes are consistent with the conclusion drawn from vibrational spectroscopy, i.e. the effective charge on the sulfur atoms in the disulfide ligand in metal complexes is between 0 and -2.

The sulfur binding energies depend upon the electronegativity of the other ligands attached to the metal. This is illustrated by the higher sulfur binding energy for  $Nb_2(S_2)_2Cl_4$  compared to  $Nb_2(S_2)_2Br_4$  and for  $Mo_3S(S_2)_3Cl_4$  compared to  $[Mo_3S(S_2)_6]^{2-}$  (Table 1.2). For each pair the metal binding energy is nearly identical [134]. Taken together the metal and sulfur binding energies indicate that the disulfide ligand is an effective electron donor to the metal, and that donation from the disulfide ligand increases as the electronegativity of the other ligands increases.

Additional evidence about the oxidation state of the sulfur can be obtained by comparison of the metal binding energies in complexes in known oxidation states. The Mo binding energies of  $[Mo_2(S_2)_6]^{2-}$  can be understood only if the ligands are formulated as  $(S_2)^{2-}$  units rather than neutral

Table 1.2  $S_{2p}$  binding energies of sulfur in polysulfido complexes

Complex	$S_{2p}$ binding energy (eV)	Ref.
$Nb_2(S_2)_2Cl_4$	164.1	134
$Nb_2(S_2)_2Br_4$	163.2	134
$(NH_4)_2[Mo_2(S_2)_6]$	163.9	134
$(NH_4)_2[Mo_3S(S_2)_6]$	163.5	134
$Mo_3S(S_2)_3Cl_4$	164.4	134
$Cp_2Mo(S_2)$	163.2	134
$MoO(S_2)(dte)_2$	163.2	134
$(NMe_4)_2[Mo_2O_2S_2(S_2)_2]$	163.2	134
$(NH_4)K[Mo_4(NO)_4(S_2)_6O]$	162.9	134
$(NH_4)_4[Mo_4(NO)_4(S_2)_5S_3]$	163.6	134
$(NH_4)_2[Pt(S_5)_3]$	164.8	139

$S_2$  fragments [143]. Similar results are found for the metal binding energies of Ir and Os complexes of disulfide ligands [4,144].

In summary, both the sulfur and metal XPS results are consistent with the disulfide ligand having an effective negative charge of about -2. The XPS results of  $[Pt(S_5)_3]^{2-}$  also suggest that the effective charge on the pentasulfide ligand is about -2 [139]. However, neither the sulfur nor the metal XPS data are sufficiently sensitive to distinguish among the various models of coordination of  $S_x^{2-}$  ligand (vide infra). A recent XPS survey of several molybdenum complexes with a variety of sulfur ligands shows that the range of  $S_{2p}$  binding energies for sulfide and thiolate ligands is only  $\sim 1$  eV [145].

### (iii) Electron absorption spectra

Table 1.3 lists the electronic absorption maxima for polysulfido complexes. The longest wavelength band in the complexes  $Cp_2Nb(S_2)X$  ( $X = Cl, Br, I$ ) and  $MoO(S_2)(dte)_2$  is assigned to be originating from ligand to metal charge transfer [146]. This assignment is probably also correct for other disulfido complexes which contain the metal atoms in a high oxidation state, e.g.,  $[Mo_2O_2S_2(S_2)_2]^{2-}$ . The position of this first band in disulfido complexes is influenced by the oxidation state and the mode of bonding of the disulfide ligand. Accurate assignments have not been made

Table 1.3. Electronic absorption bands in polysulfide complexes

Complex	Color	Band maxima (nm)	Ref.
$\text{Cp}_2\text{Nb}(\text{S}_2)\text{Cl}$	Red	272, 368, 483	88
$\text{Cp}_2\text{Nb}(\text{S}_2)\text{Br}$	Dark red	286, 372, 474	88
$\text{Cp}_2\text{Nb}(\text{S}_2)\text{I}$	Violet	290, 372, 469	88
$\text{MoO}(\text{S}_2)(\text{dtc})_2$	Blue	394, 581	26
$[\text{MoO}_2\text{S}_2(\text{S}_2)_2]^{2-}$	Red-orange	278, 305, 370, 463	134
$\text{Mo}_2(\text{S}_2)_6\text{Cl}_6$	Dark brown	365, 474, 763	134
$[\text{Mo}_2(\text{S}_2)_6]^{2-}$	Black-green	313, 357, 417, 500, 625, 769	134
$\text{Mo}_3\text{S}(\text{S}_2)_3\text{Cl}_4$	Red	370, 500	134
$[\text{Mo}_3\text{S}(\text{S}_2)_6]^{2-}$	Red	333, 370, 465, 541	134
$\text{Nb}_2(\text{S}_2)_2\text{Cl}_4$	Brown	232, 270, 345, 385, 455, 556, 667	134
$\text{Nb}_2(\text{S}_2)_2\text{Br}_4$	Red brown	232, 345, 385, 455, 556	134
$[\text{Mo}_4(\text{NO})_4(\text{S}_2)_6\text{O}]^{2-}$	Violet	455, 532, 588, 714	134
$[(\text{NH}_3)_5\text{Ru}(\text{S}_2)-\text{Ru}(\text{NH}_3)_5]^{4-}$	Green	221, 285, 412, 704	86
$\{\text{Cr}(\text{S}_2)\text{Cr}\}^{4+}$	Yellow brown	303, 400	72

...contd.

[Table 1.3 contd.]

Complex	Color	Band maxima (nm)	Ref.
$[(\text{CN})_5\text{Co}(\text{S}_2)-\text{Co}(\text{CN})_5]^{6-}$	Red-brown	258, 313, 370, 526, 645	29
$\text{Cp}_2\text{Fe}_2(\text{S}_2)-(\text{SEt})_2$	Dark green	233, 309, 478, 599, 840	108
$[\text{Ni}(\text{S}_4)_2]^{2-}$	Black	300, 365, 469, 671	43
$[\text{MoS}(\text{S}_4)_2]^{2-}$	Red brown	316, 340, 405, 470	11
$[\text{MoO}(\text{S}_4)_2]^{2-}$	Green	316, 475, 555	11
$[\text{Pt}(\text{S}_5)_3]^{2-}$	Red	<190, 290, 390	56
$[\text{Pt}(\text{S}_5)_2]^{2-}$	Red	<200, 233, 476	56
$[\text{Fe}_2\text{S}_2(\text{S}_5)_2]^{2-}$	Red brown	370, 445, 600	77
$[(\text{S}_5)\text{FeS}_2\text{MoS}_2]^{2-}$	Brown	305, 340, 410, 480, 545, 605	78
$[\text{Hg}(\text{S}_6)_2]^{2-}$	Orange	285, 350, 402	60
$[\text{Cu}_3(\text{S}_6)_3]^{3-}$	Red	285, 350, 430	59

in the case of other polysulfido complexes. However, it is proposed that the intense high energy transition in  $(\text{Et}_4\text{N})_2^-[(\text{S}_4)_2\text{MoS}]$  and  $(\text{Et}_4\text{N})_2[(\text{S}_4)_2\text{MoO}]$  (Table 1.3) is very likely due to an internal ligand transition associated with  $\text{S}_4^{2-}$  ligands. The transitions occurring at longer wavelength are tentatively assigned to  $\text{S}_4^{2-} \rightarrow \text{Mo}$  charge-transfer absorptions [11].

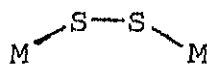
#### D. Structural Chemistry

The known polysulfido complexes show an astonishing variety of structures owing to the ability of these ions to coordinate in a number of ways.

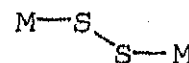
In disulfido complexes this variety results from extension of the fundamental structures Ia (side on coordination) and IIa and IIb (cis and trans end-on bridging coordination), by using the remaining lone pairs of electrons on sulfur to coordinate additional metal atoms [2]:



Ia



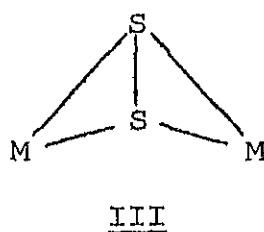
IIa (cis)



IIa (trans)

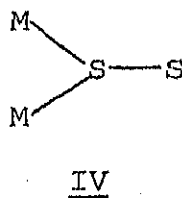
Such coordination of additional metal atoms occurs for all three fundamental structural types (Ia, IIa and IIb), and representative examples of all of the known structures are summarized in Table 1.4.

Another type of structural unit found in many disulfido-metal cluster compounds is III, in which both sulfur atoms of the disulfide ligand are bonded to each of two metal atoms




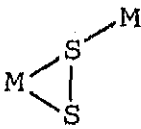
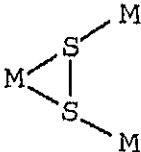
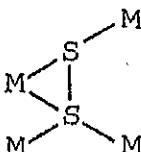
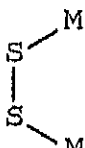
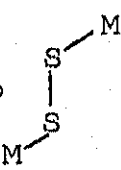
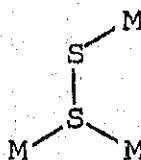
The S-S bond is oriented approximately normal to the metal-metal vector.

Very recently a new type of bridging disulfide ligand was discovered in which two metal atoms are attached to the same atom of the ligand (structural type IV):



Structures of two closely related trisulfido complexes  $[(\text{Me}_5\text{C}_5)_2\text{TiS}_3]$  and  $[(\text{MeC}_5\text{H}_4)_2\text{TiS}_3]_2$  have been determined by X-ray crystallography [38,82]. In the first compound the disulfide ligand forms a nonplanar four-membered ring with the metal atom (Fig. 1.2a). The dimeric  $[(\text{MeC}_5\text{H}_4)_2\text{TiS}_3]_2$  has two bridging  $\text{S}_3^{2-}$  ligands which together with the metal atom form an eight-membered  $\text{Ti}_2\text{S}_6$  ring (Fig. 1.2b). In both the

Table 1.4. Typical geometries of disulfido complexes

Structural type	Example	(S-S) Bond Length (pm)	Ref,
Ia 	$[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$	207	3, 147
Ib 	$[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$	205	30
Ic 	$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{15}$	207	97, 148
Id 	$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{15}$	209	97, 148
IIa 	$\text{Cp}_2\text{Fe}_2(\text{S}_2)(\text{SEt})_2$	202	92, 149
IIb 	$[(\text{NH}_3)_5\text{Ru}(\text{S}_2)\text{Ru}(\text{NH}_3)_5]^{4+}$	201	86, 150
IIc 	$\text{Cp}_4\text{Co}_4(\text{S}_2)_2\text{S}_2$	201	19

...contd.



[Table 1.4 contd.]

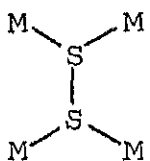
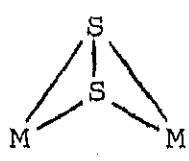
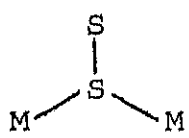
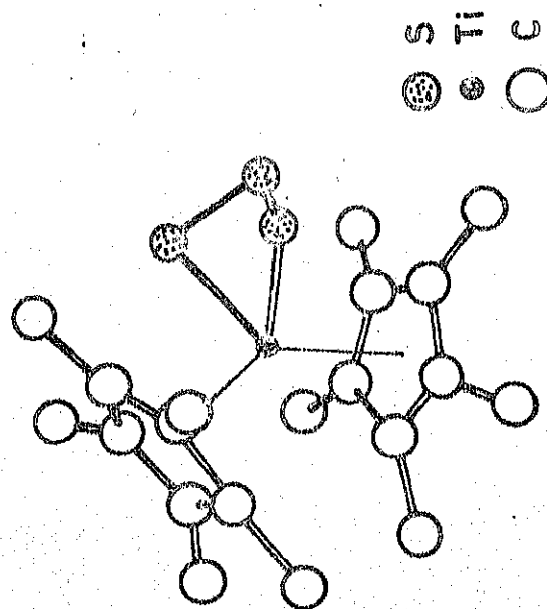
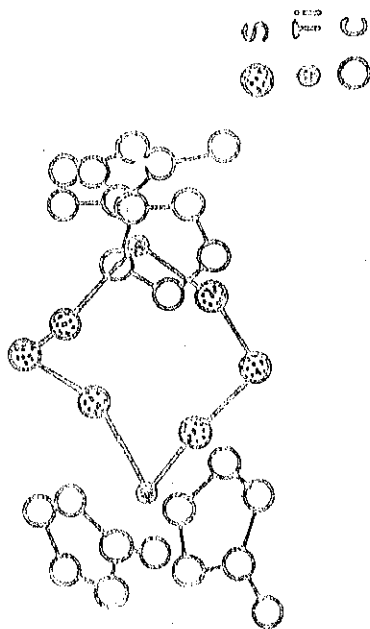
Structural type	Example	(S-S) Bond Length (pm)	Ref.	
IIId		$\left\{ \text{SCo}_3(\text{CO})_7 \right\}_2 (\text{S}_2)$	204	20, 27
III		$[\text{Mo}_2(\text{S}_2)_6]^{2-}$	204	31, 151
IV		$\text{Cp}_2\text{Cr}_2(\text{S}_2)_2\text{S}$	210	152

Table 1.5. Bond distances and bond angles in the trisulfido complexes

Compound	Bond distances (pm)		Bond angles (deg.)			Ref.
	Ti-S	S-S	Ti-S-S	S-S-S	S-Ti-S	
$(\text{Me}_5\text{C}_5)_2\text{TiS}_3$	241.3	204.1	76.34	105.30	84.44	38
$[(\text{MeC}_5\text{H}_4)_2\text{TiS}_3]_2$	241.6	205.8	116.93	109.07	96.08	82



(a)



(b)

FIG. 1.2 STRUCTURES OF (a)  $[\text{Me}_5\text{C}_5/2\text{TiS}_3]$  AND (b)  $[\text{MeC}_5\text{H}_4/2\text{TiS}_3]_2$

compounds the metal atom has an approximate tetrahedral geometry. The bond distances and bond angles are listed in Table 1.5.

Formation of a nonplanar five-membered  $MS_4$  ring is the most common structural variety found in tetrasulfido complexes. As representative examples structures of  $[NiS_8]^{2-}$  and  $[Mo_2S_{10}]^{2-}$  are shown in Figs. 1.3(a) and 1.3(b). Bond lengths for some of the compounds for which structures are known are given in Table 1.6. The M-S bond lengths in these compounds are comparable to the M-S bond lengths observed in other sulfur ligated compounds of these metals. But there is a distinct variation in the S-S bond lengths when compared to the S-S bond length in  $BaS_4 \cdot H_2O$  (Table 1.6). The outer S(1)-S(2) and S(3)-S(4) bonds are longer than the central S(2)-S(3) bond. However, in most of the complexes bond distances lie in the range expected for sulfur rings and those found in other polysulfido compounds. The alternations in the S-S bond lengths have been rationalized in terms of significant  $M(d\pi)-S(d\pi)$  interactions which perturb the  $S(d\pi)-S(d\pi)$  bonding between central sulfur atoms [130]. However, extended Hückel molecular orbital calculations on these molecules suggest that  $d\pi-d\pi$  bonding effects are not an important contributor to the observed alternation in bond lengths [130].

The S-S-S bond angles (Table 1.7) in most of the compounds are in the range of the reported values for  $S_8$  rings [156] suggesting the presence of less ring strain.

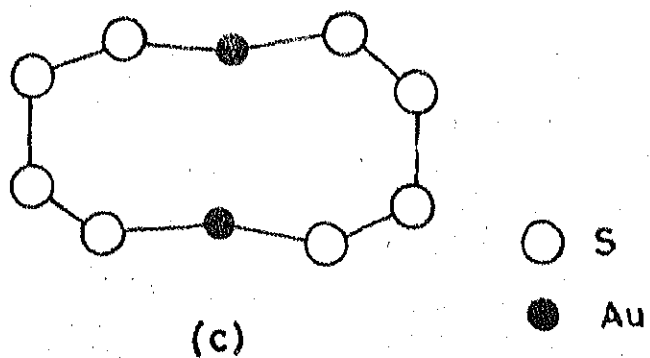
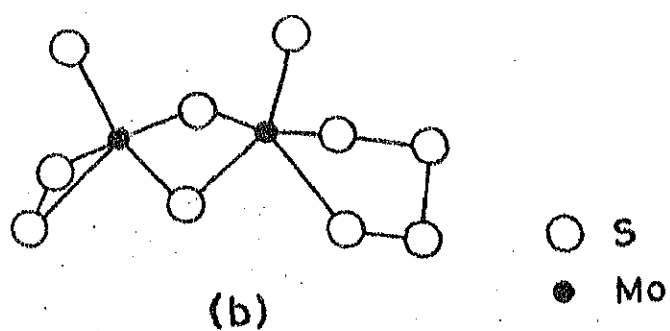
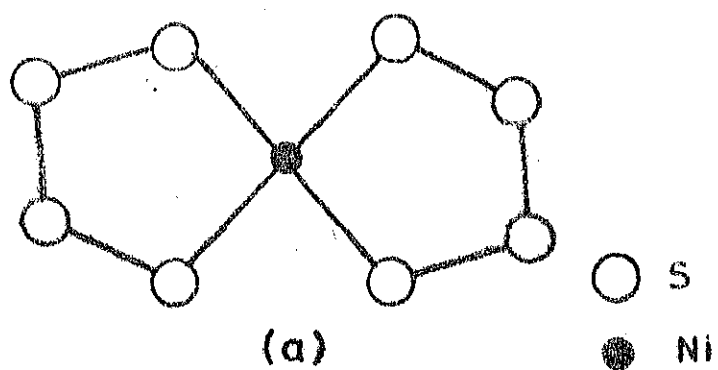
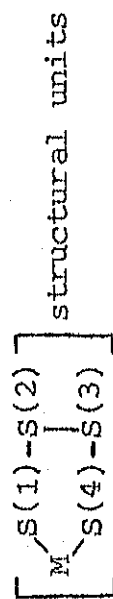


FIG. 1.3 STRUCTURES OF (a)  $[\text{Ni}(\text{S}_4)_2]^{2-}$   
(b)  $[\text{Mo}_2\text{S}_{10}]^{2-}$  AND (c)  $[\text{Au}_2\text{S}_8]^{2-}$

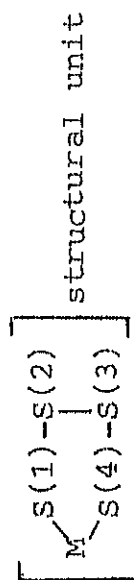
Table 1.6. Bond lengths of S-S and M-S bonds in compounds with MS<sub>4</sub>



Compound	Bond Distances (pm)					Ref.
	S(1)-S(2)	S(2)-S(3)	S(3)-S(4)	M-S(1)	M-S(4)	
BaS <sub>4</sub> ·H <sub>2</sub> O*(a)	206.9	206.3	206.9	-	-	153
BaS <sub>4</sub> ·H <sub>2</sub> O*(b)	207.9	206.2	207.9	-	-	153
(AsPh <sub>4</sub> ) <sub>2</sub> [Mo <sub>2</sub> S <sub>10</sub> ] <sup>**</sup> (a)	201.9	197.0	211.9	240.3	240.9	81
(AsPh <sub>4</sub> ) <sub>2</sub> [Mo <sub>2</sub> S <sub>10</sub> ] <sup>**</sup> (b)	216.9	193.6	209.6	240.3	240.9	81
(Et <sub>4</sub> N)[MoS <sub>9</sub> ]	216.6	201.2	210.7	233.3	238.7	11, 76
(Et <sub>4</sub> N) <sub>2</sub> [MoOS <sub>8</sub> ]	215.9	200.8	212.0	236.3	239.5	11
(PPh <sub>4</sub> ) <sub>2</sub> [Mo <sub>2</sub> S <sub>12</sub> ]	204.9	202.5	205.3	226.0	238.7	11
Pt(S <sub>4</sub> )(dppe)	206.9	201.2	204.7	232.7	234.4	130
Pt(S <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	202.4	202.2	208.1	236.0	236.6	84
Cp <sub>2</sub> Mo(S <sub>4</sub> )	208.5	201.8	208.1	245.5	245.1	154
Cp <sub>2</sub> W(S <sub>4</sub> )	210.5	201.6	211.6	241.3	241.3	155
(Et <sub>4</sub> N) <sub>2</sub> [NiS <sub>8</sub> ]	207.3	203.7	-	218.5	-	43

\*The molecule has two crystallographically different S<sub>4</sub> units (a and b).

\*\*The MS<sub>4</sub> ring is disordered with (a) the major component and (b) the minor one.

Table 1.7. Bond angles in compounds with  $MS_4$ 

Compound	Bond angles (deg.)							Ref.
	M-S(1)-S(2)	S(1)-S(2)-S(3)	S(2)-S(3)-S(4)	S(3)-S(4)-M	S(1)-M-S(4)			
$BaS_4 \cdot H_2O^*(a)$	-	104.3	104.3	-	-			153
$BaS_4 \cdot H_2O^*(b)$	-	104.0	104.0	-	-			153
$(AsPh_4)_2[Mo_2S_{10}]^{**}(a)$	110.5	102.1	105.8	97.1	85.1			81
$(AsPh_4)_2[Mo_2S_{10}]^{**}(b)$	104.0	81.5	100.4	109.7	85.1			81
$(Et_4N)_2[MoS_9]$	112.3	100.2	101.8	103.6	90.3			11,76
$(Et_4N)_2[MoOS_8]$	111.7	100.8	101.9	103.6	90.4			76
$(PPh_4)_2[Mo_2S_{12}]$	111.7	103.4	98.4	99.6	89.7			76
$Pt(S_4)(dppe)$	104.5	99.8	101.0	102.9	95.3			130
$(Et_4N)_2[NiS_8]$	105.1	99.4	-	-	99.1			43
$Cp_2Mo(S_4)$	108.8	100.8	99.9	108.4	88.2			154
$Cp_2W(S_4)$	109.1	101.0	100.1	109.2	89.1			155

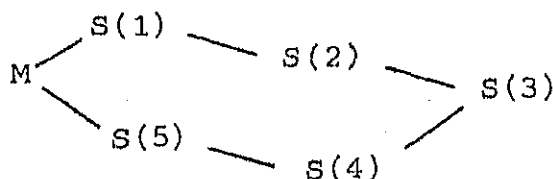
\*The molecule has two crystallographically different  $S_4$  units.

\*\*The  $MS_4$  ring is disordered with (a) the major component and (b) the minor one.

Instead of forming a  $MS_4$  ring, the two end sulfur atoms of the  $S_4^{2-}$  ligand can coordinate to two metal atoms forming a sulfur bridge. This structural variety is found in  $[Au_2S_8]^{2-}$  where the two  $S_4^{2-}$  ligands form with the metal a ten-membered heterocyclic ring (Fig. 1.3b) [39].

Multiple coordination by the end sulfur atoms of the tetrasulfide ligand leads to metal sulfur clusters. Examples are  $[Cu_3(S_4)_3]^{3-}$ ,  $[Cu_6(S_4)_3(S_5)]^{2-}$  (Fig. 1.4a and 1.4b) [17, 44, 45] and  $[Cu_4S_x]^{2-}$  ( $x = 13-15$ ) [39].

The most common structural type for  $S_5^{2-}$  ligand, like for other polysulfides is the formation of a six-membered  $MS_5$  ring in the chair conformation.



As representative examples structures of  $[PtS_{15}]^{2-}$  [157, 158],  $[Fe_2S_{12}]^{2-}$  [77] and  $Cp_2TiS_5$  [158] are shown in Fig. 1.5.  $[PtS_{15}]^{2-}$  consists of three six-membered  $MS_5$  rings and provides an interesting example of a purely inorganic compound which is optically active. This compound has been resolved recently [160].

In  $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$  [54] the two end sulfur atoms of the  $S_5^{2-}$  are coordinated to separate molybdenum centers, thus forming a sulfur bridge between the molybdenum atoms

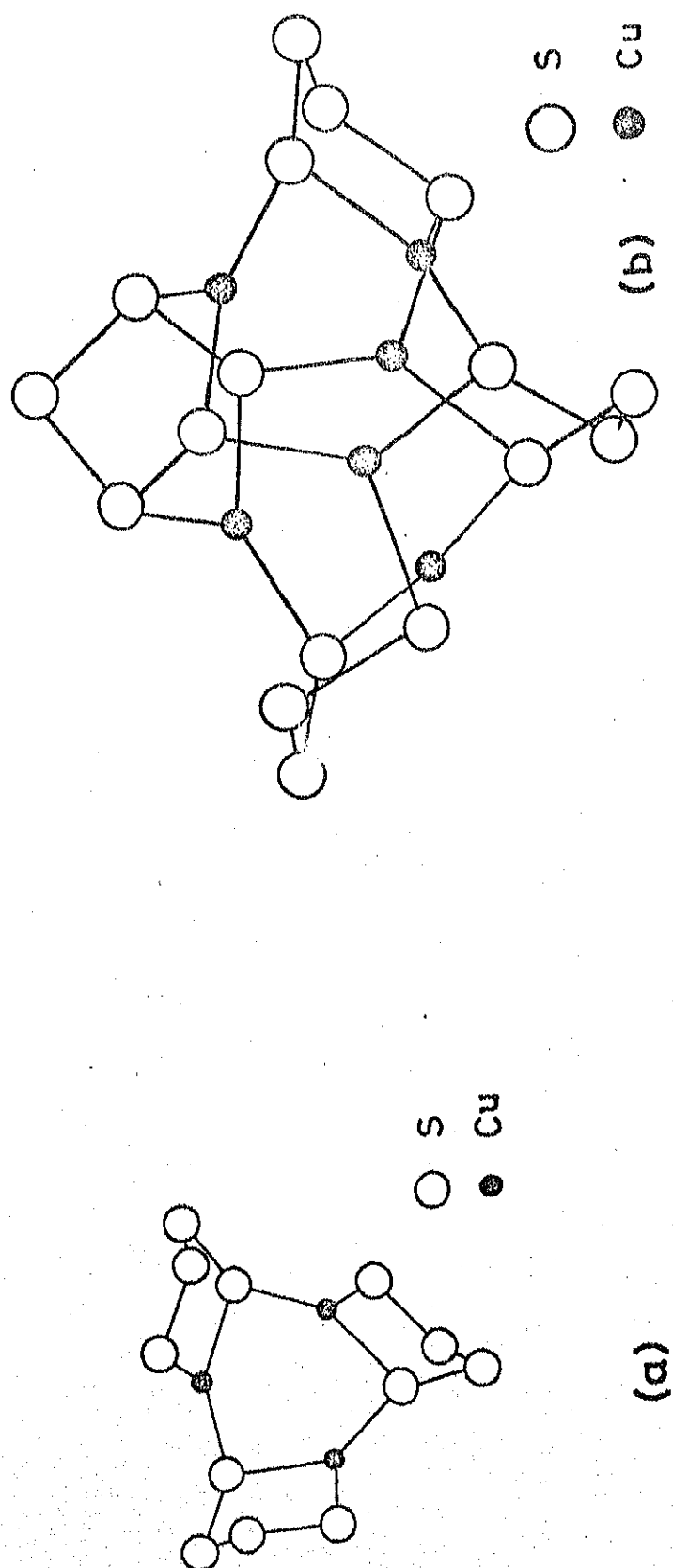


FIG.1.4 STRUCTURES OF (a)  $[\text{Cu}_3\text{S}_{12}]^{3-}$  AND (b)  $[\text{Cu}_6\text{S}_{17}]^{2-}$



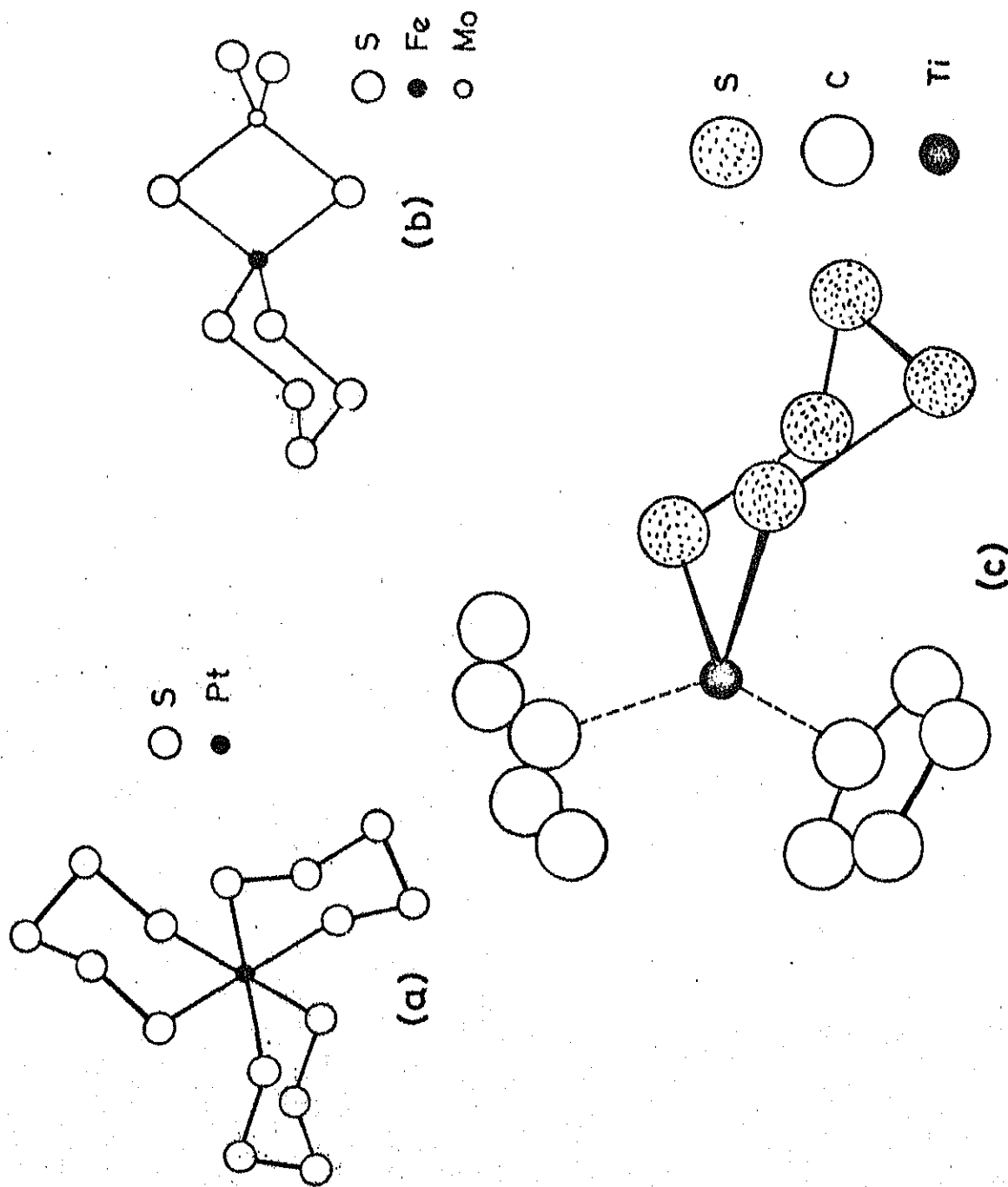


FIG. 1.5 STRUCTURES OF (a)  $[\text{Pt S}_{15}]^{2-}$  (b)  $[(\text{S}_5)\text{Fe S}_2\text{Mo S}_2]^{2-}$  AND (c)  $[(\text{C}_5\text{H}_5)_2\text{Ti S}_5]$

[Fig. 1.6a]. This compound also has two terminal and one bridging  $S_2^{2-}$  ligands. One structural aspect of particular interest here is that the eight-membered heterocyclic moiety  $(S_5)Mo_2(S_2)$  has practically the same geometry as that of cyclo-octasulfur.

Another variety of bridge formation by  $S_5^{2-}$  ligand is found in  $[Os_2(S_5)(S_3CNET_2)(S_2CNET_2)_3]$  [15]. Here  $S_5^{2-}$  forms a  $MS_5$  ring with one of the Os atoms, in addition, one of the terminal sulfur of the  $S_5^{2-}$  coordinates to the other Os atom, thus forming a bridge.

In polynuclear metal aggregates an extension of the above structural types leads to some interesting structural features. In  $[Cu_4(S_5)_3]^{2-}$  and  $[Cu_4(S_4)(S_5)_2]^{2-}$  the  $S_5^{2-}$  is coordinated to three different copper atoms (Fig. 1.6b) [39]. With one copper atom it forms a six-membered ring, in addition each of the end sulfur atom coordinates to a different copper atom leading to a copper-sulfur cluster.

In  $[Cu_6S_{17}]^{2-}$  [17,45] a novel  $S_5^{2-}$  coordination occurs (Fig. 1.4b). Four sulfur atoms of the pentasulfide ligand are involved in bonding with four different copper atoms. The two terminal sulfur atoms S(1) and S(5) each coordinate to two different copper atoms while S(2) and S(4) coordinate to one copper atom each. In addition, this compound has three  $S_4^{2-}$  ligands (vide supra).

Bond lengths and bond angles of a few pentasulfido complexes are listed in Table 1.8 and 1.9. An obvious interest is a comparison of the molecular parameters of these hetero-atom ring systems with those of cyclohexasulfur,  $S_6$ . An X-ray diffraction study of this sulfur allotrope [161], yielded for the chain like molecules S-S bond length of 205.7 pm and a S-S-S bond angle of  $102.2^\circ$ . It is obvious that a formal substitution of a metal atom in place of one sulfur atom produces deformation on the ring parameters. The much larger M-S distances compared to the S-S bond lengths are compensated to a large extent by the smaller S-M-S angle, such that the geometry of the resultant  $MS_5$  ring is not appreciably altered from that of  $S_6$ . The greatest deformation expectedly involves, the two sulfur atoms S(1) and S(5), directly bonded to the metal atom. The variations in the S-S bond lengths are small and the average S-S bond length in most of the complexes fall very close to that of  $S_6$ . The S-S-S bond angles are slightly higher than in  $S_6$  and quite a bit higher than those reported for  $S_8$  (98.3 - 100.6) [156]. Therefore,  $MS_5$  rings in these complexes might be experiencing considerable ring strain. In  $MS_4$  ring containing complexes, however, the S-S-S angles are very much comparable to those of  $S_8$  thus implying less strain on the ring. This difference in the strain energies may be a contributing factor to the observation that  $[Pt(S_5)_3]^{2-}$  reacts with  $PPh_3$  to give  $Pt(S_4)(PPh_3)_2$ , which has a smaller  $MS_4$  ring (vide supra) [83].

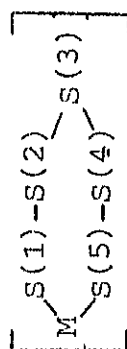


Table 1.8. Bond lengths of S-S and M-S bonds in pentasulfido complexes

Compound	Bond Length (pm)						Ref.
	S(1)-S(2)	S(2)-S(3)	S(3)-S(4)	S(4)-S(5)	M-S(1)	M-S(5)	
$(\text{NH}_4)_2[\text{Pt}(\text{S}_5)_3] \cdot 2\text{H}_2\text{O}^{\text{a}}$	204.0	202.6	205.9	202.1	240.1	237.8	158
$\text{K}_2[\text{Pt}(\text{S}_5)_3]^{\text{a}}$	204.4	201.8	201.8	200.0	238.9	233.2	46
$\text{Cp}_2\text{Ti}(\text{S}_5)^{\text{b}}$	206.5	203.6	204.9	204.4	244.1	241.0	12
$\text{Cp}_2\text{Ti}(\text{S}_5)^{\text{b}}$	205.9	205.6	204.7	205.9	244.8	242.2	12
$\text{Cp}_2\text{V}(\text{S}_5)$	205.1	206.2	205.5	204.3	246.4	245.0	12
$(\text{NH}_4)_3[\text{Mo}_2(\text{NO})_2(\text{S}_2)_3(\text{S}_5)\text{OH}]^{\text{c}} \cdot 2\text{H}_2\text{O}$	206.4	206.1	205.5	205.5	248.5	247.5	54
$\text{Os}_2(\text{S}_5)(\text{S}_3\text{CNET}_2)(\text{S}_2\text{CNET}_2)_3^{\text{d}}$	206.0	207.0	206.0	216.0	227.3, 227.1	244.3	15

a. Values are given for only one  $\text{PtS}_5$  ring.

b. The compound has two different monoclinic crystalline phases.

c. The two terminal sulfur atoms are connected to two different molybdenum atoms.

d. One terminal sulfur atom S(1) is connected to two Os atoms.

Table 1.9 Bond angles in  $MS_5$  ring of pentasulfido complexes

Compound	Bond angles (deg.)						Ref.
	S(1)MS(5)	MS(1)S(2)	MS(5)S(4)	S(1)S(2)S(3)	S(2)S(3)S(4)	S(3)S(4)S(5)	
(NH <sub>4</sub> ) <sub>2</sub> [Pt(S <sub>5</sub> ) <sub>3</sub> ]- ·2H <sub>2</sub> O <sup>a</sup>	92.0	109.8	111.7	108.4	100.7	106.3	158
K <sub>2</sub> [Pt(S <sub>5</sub> ) <sub>3</sub> ] <sup>a</sup>	94.6	105.6	110.2	107.8	103.5	103.7	46
[Cp <sub>2</sub> Ti(S <sub>5</sub> )] <sup>b</sup>	95.0	107.9	109.3	105.3	106.9	103.1	12
[Cp <sub>2</sub> Ti(S <sub>5</sub> )] <sup>b</sup>	94.6	107.4	108.6	105.2	106.7	102.7	12
[Cp <sub>2</sub> W(S <sub>5</sub> )]	89.4	113.9	112.0	105.1	104.4	105.4	12

a, Values for only one  $PtS_5$  ring are given.

b, The molecule has two distinct monoclinic crystalline phases.

Hexasulfide,  $S_6^{2-}$  is also found to coordinate in various ways.  $(NH_4)_2[PdS_{11}]^{2-} \cdot 2H_2O$  has a polymeric structure bridged by  $S_6^{2-}$  chains [58]. Complexes are also known where it forms seven-membered  $MS_6$  rings. Examples are  $[Hg(S_6)_2]^{2-}$  (Fig. 1.7a) [60],  $[Ag_2S_{20}]^{4-}$  (Fig. 1.7b) [62] and  $[Cu_2S_{20}]^{4-}$  [44]. In  $[Cu_3(S_6)_3]^{3-}$  (Fig. 1.8a) and  $[Ag_2(S_6)_2]^{2-}$  (Fig. 1.8b) [59,61] multiple coordination by  $S_6^{2-}$  leads to trimeric and dimeric structures, respectively.

So far only two compounds with a coordinated  $S_8^{2-}$  unit are known. In both these compounds,  $[Cu_2S_{20}]^{4-}$  [44] and  $[Ag_2S_{20}]^{4-}$  (Fig. 1.7b) [62],  $S_8^{2-}$  acts as a bridge between two  $MS_6$  moieties.

The structure of the nonasulfido complex,  $[AuS_9]^-$  is shown in Fig. 1.8c [63]. The ligand  $S_9^{2-}$ , forms with gold, a ten-membered heterocyclic ring. The structure of the  $[AgS_9]^{2-}$  is reported to be similar [61].

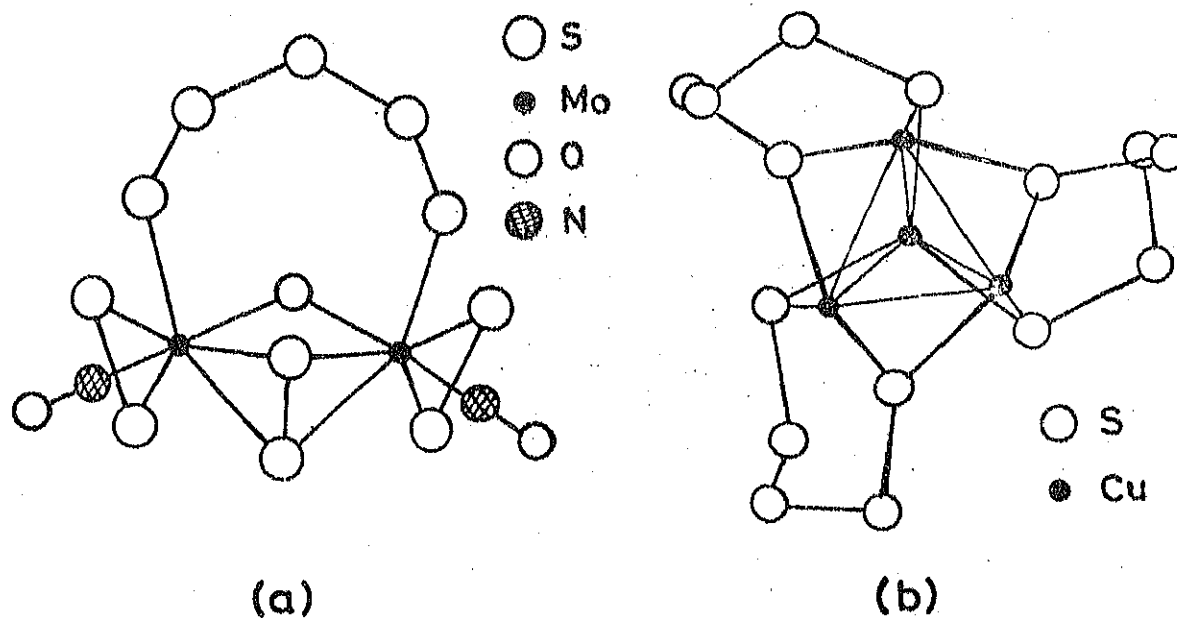


FIG. 1.6 STRUCTURES OF (a)  $[\text{Mo}(\text{NO})_2(\text{S}_2)_3(\text{S}_5)\text{OH}]^{3-}$  AND (b)  $[\text{Cu}_4(\text{S}_5)_3]^{2-}$

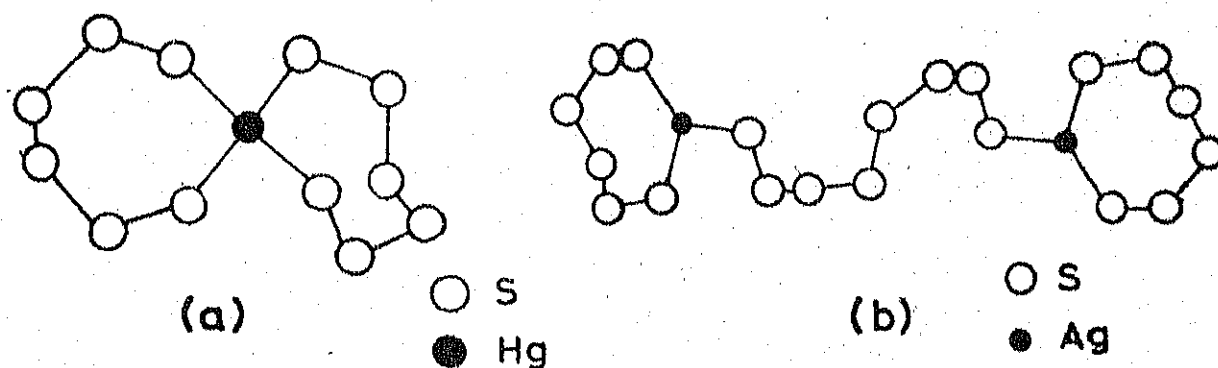


FIG. 1.7 STRUCTURES OF (a)  $[\text{Hg}(\text{S}_6)_2]^{2-}$  AND (b)  $[(\text{S}_6)\text{Ag}(\text{S}_8)\text{Ag}(\text{S}_6)]^{4-}$

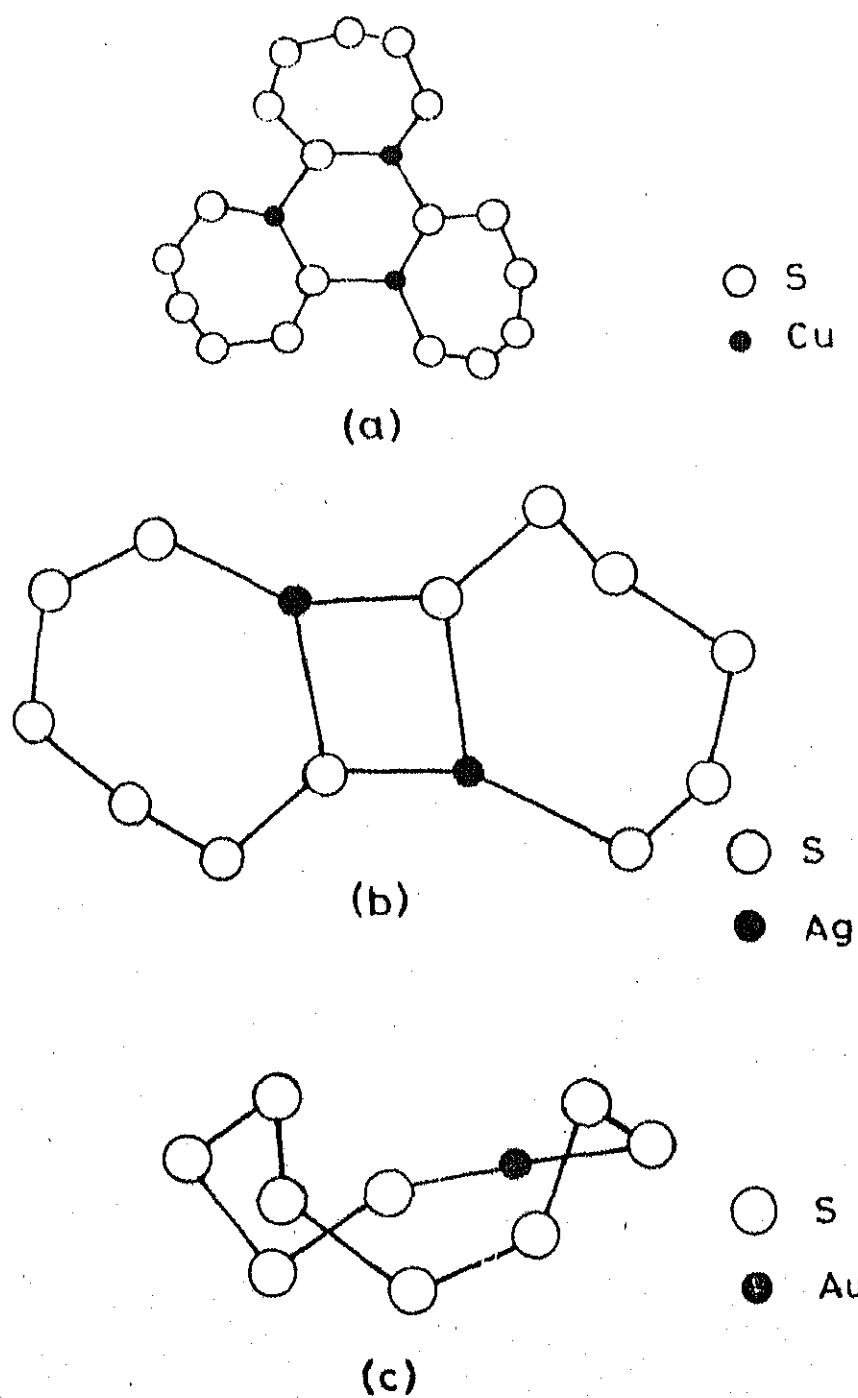


FIG. 1.8 STRUCTURES OF (a)  $[\text{Cu}_3(\text{S}_6)_3]^{3-}$   
 (b)  $[\text{Ag}_2(\text{S}_6)_2]^{2-}$  AND (c)  $[\text{AuS}_9]^-$



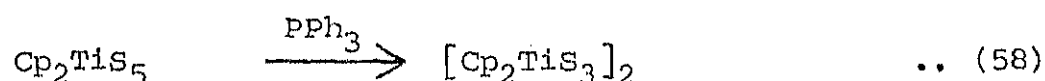
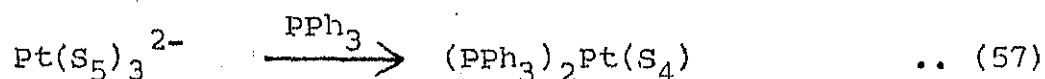
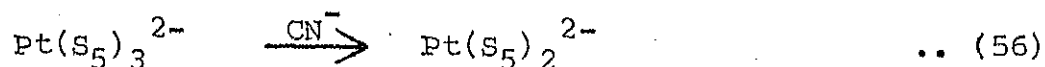
CHAPTER 2

## SCOPE OF THE WORK

The first polysulfido complex synthesized is of platinum,  $[\text{Pt}(\text{S}_5)_3]^{2-}$  [1], however, no systematic approaches have been made to know about the polysulfido complexes of its lower congeners, viz., palladium and nickel. A study of the interactions of polysulfide with these metals is important considering the fact that nickel, palladium and platinum compounds are used as catalysts in many reactions of industrial importance [162]. In addition there is great interest in metal-sulfur interactions because of the catalyst poisoning properties of sulfur compounds. Furthermore, a systematic study of these compounds can also provide insight concerning synthetic and theoretical aspects of sulfur chemistry.

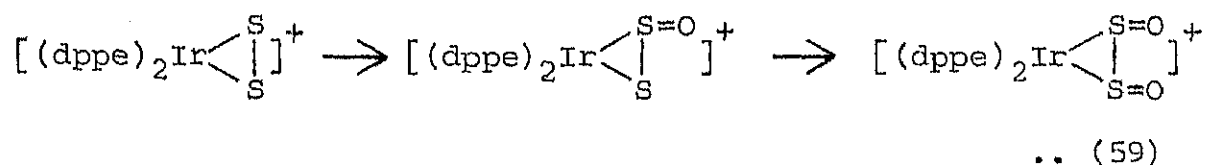
Examples of polysulfide  $\text{S}_x^{2-}$ , coordinated to metal centers are known for a wide variety of metals. However,

the factors that determine the chain length and ring size are poorly understood. Also the factors which determine the interconversion between two rings are not clearly known. For example, in reactions (56) to (58) [56,82,83]:

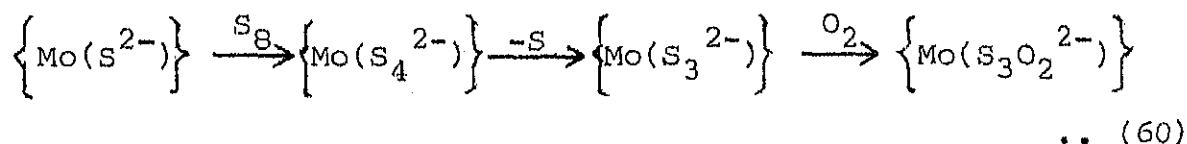


sulfur abstraction by a nucleophile leads to different products. Particularly in reaction (58) a dimeric compound with  $\text{S}_3^{2-}$  bridges is formed. The corresponding monomeric compound with a  $\text{TiS}_3$  ring is also known, but is prepared by a different synthetic methodology [38]. It is interesting to note that the same nucleophile,  $\text{PPh}_3$  reacts with  $\text{PtS}_5$  ring in a different manner giving  $\text{PtS}_4$  ring [83]. As of now, the reasons for this diversity are not known.

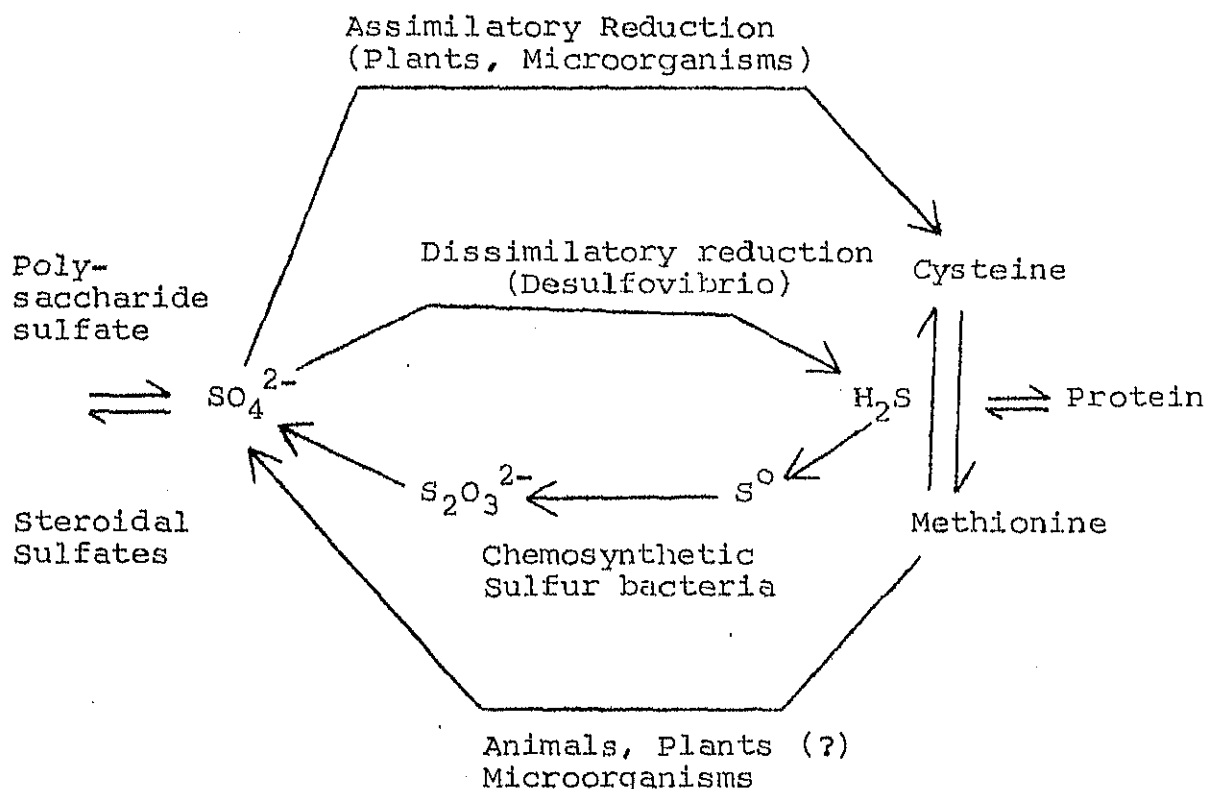
Another fascinating aspect of the polysulfido metal complexes is that they undergo very unusual redox reactions. Most of the times the oxidation or reduction takes place at the metal center (for example, see Eqns. (56) and (57)). But the most interesting reactions are the ones where the oxidation of one or more sulfur atoms of the coordinated  $\text{S}_x^{2-}$  takes place. For example, see Eqn. (59) [110,111]:



This type of redox reaction is important because species hitherto unknown in free or coordinated states can be generated and stabilized by the stepwise oxidation of the coordinated sulfur. The synthesis of the complex containing coordinated  $S_3O_2^{2-}$  ion is also believed to be formed via the oxidation of coordinated  $S_x^{2-}$  ligand [Eqn. (60)] [112]:



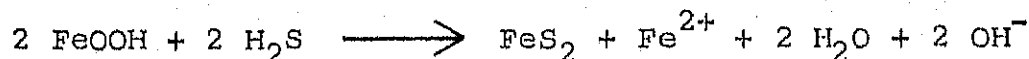
These kind of reactions are also important for an understanding of the redox reactions of the sulfur cycle. The oxidation of  $S^{2-}$  to  $SO_4^{2-}$  and the reverse reduction  $SO_4^{2-}$  to  $S^{2-}$  balance the sulfur in our ecosystem. It is understood that the formation of sulfur containing biomolecules are dependent on the different stages of this cycle. In biological process the cycle can be represented as [163]:



The reaction involving changes of eight electrons in the overall cycle using metal clusters is thus very important. If one assumes that some metalloenzymes catalyze this reaction, then whether the electron transfer in the substrate is in a stepwise manner or at a time, is difficult to rationalize in a straightforward manner. However, in the sulfur cycle, formation of the intermediate species like neutral sulfur ( $\text{S}^0$ ) and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) before the final oxidation to sulfate ( $\text{SO}_4^{2-}$ ) strongly suggest that the redox reactions are most likely to be in a stepwise manner. The formation of  $\text{S}_2\text{O}_3^{2-}$  is proposed to be due to the interaction of  $\text{SO}_3^{2-}$  with  $\text{S}^0$ , which is formed in the first oxidation step

of  $S^{2-}$ . Similarly one can concede the idea that the  $S^0$  formed can also interact with  $S^{2-}$  to generate  $S_x^{2-}$ . The existence of  $S_x^{2-}$  containing compounds of transition metals in minerals and the ready formation of  $S_x^{2-}$  complexes of metals by simply interacting sulfur with metal or metal salts at high temperature and pressure or simple metal compounds with aqueous polysulfide suggest that the polysulfide containing compounds might play a role in this sulfur cycle.

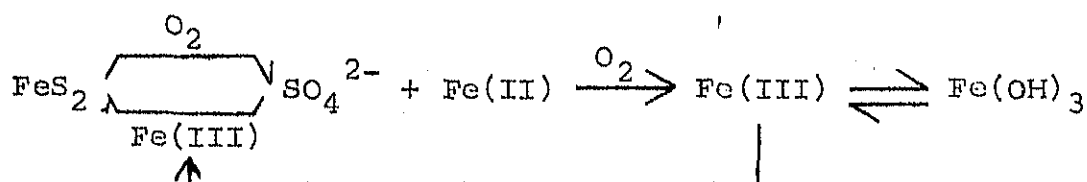
The interesting oxidations of the bound  $S_x^{2-}$  and the isolation of complex containing  $S_2O^{2-}$ ,  $S_2O_2^{2-}$  and  $S_3O_2^{2-}$  have opened a newer line of approach to the oxidative part of the sulfur cycle. One can also speculate that these  $S_xO_y^{2-}$  types of species could be possible intermediates in the oxidation of  $S^{2-}$  to  $SO_4^{2-}$  during the sulfur cycle. The ultimate fate of most of the sulfide in marine sediments is to form pyrite ( $FeS_2$ ). Two possible mechanisms suggested for its formation are [164]:



Sulfide and oxygen may coexist in aqueous solutions for relatively long periods of time. The lifetimes of sulfide species in oxygen saturated sea water (pH 8) are in the order of a few hours. Unified mechanism for the autooxidation of  $H_2S$

is difficult to propose because traces of metal compounds affect significantly the autooxidation rate.

It is known that the biochemistry of sulfur cycle is dependent on iron system as catalyst. The weathering of pyrite is probably the most important oxidation process of sulfur in the lithosphere. The oxidation is proposed to follow the following reaction scheme [165]:



Fe-S system comprise a large variety of metallobiomolecules and the Fe-S proteins are mainly concerned with the electron transport system. Recently analogous to these Fe-S proteins some nickel systems have been recognized [166] and are reported to have different redox properties. The factors governing these redox properties are mainly concerned with the attachment of metal and sulfur, and their overall geometry. In recognition of the importance of Fe-S proteins several new systems comprising of iron and sulfur have been synthesized and the prospects of these systems as models of Fe-S proteins have been stressed upon [167]. Therefore, it will not be out of place to enquire partly on this aspect utilizing nickel as the metal and purely inorganic sulfur moieties as ligands. It is well known that the oxidation of iron sulfide is faster compared

to that of nickel sulfide and if one is interested to know the intermediate stages of oxidation of sulfide then nickel is obviously going to be a better choice than iron. So, viewing the scope of work in this line, it would be highly interesting if one can synthesize some polysulfido complexes of nickel and then try to isolate some of the oxidation products of the coordinated polysulfide which could be stabilized under the influence of nickel.

From the stereochemistry point of view, nickel offers a greater challenge over platinum as even in the +2 oxidation state nickel can be stabilized in tetra-, penta- as well as in hexacoordination. Furthermore, the prospects of tetrahedral and square-planar geometries in tetracoordination number as well as trigonal-bipyramid and square-pyramid geometries in pentacoordination number offers some interesting features when the primary ligands are unconventional, i.e., polysulfides and their derivatives. The dependency of the size of this metal-sulfur ring over the nature of the coligand could be a worth-trying effort utilizing newer synthetic strategies.

As platinum forms stable complexes in +4 oxidation state, efforts can be made to utilize different redox reactions to interchange the oxidation state of nickel and palladium from +2 to +4. It is known, specially for nickel that when the donor atoms are sulfur, Ni(II) species can readily undergo oxidation to give Ni(IV) species [168].

Solubility product of NiS is very low and as such interaction between Ni(II) and  $S^{2-}/S_x^{2-}$  can readily give the insoluble nickel sulfide. A judicious use of a compound containing nickel is essential here wherein there is going to be a good balance between the thermodynamic stability as well as the kinetic one so that the desired course of reaction can be achieved.

It is interesting to note that polysulfide coordinated compounds of transition metals undergo reactions with carbon disulfide and substituted acetylenes to generate perthiocarbonate and dithiolene type of ligands, respectively (cf. Chapter 1). Such type of studies have not been carried out with this group of metals, where it is known that the dithiolene type of sulfur donor ligands can stabilize these metals in three different oxidation states viz., +2, +3 and +4 [168]. The formation of these ligands from metal-polysulfide ring give elemental sulfur [122] and the involvement of this sulfur in any in situ redox process might be interesting as the dithiolene complexes of these metals undergo reversible redox reactions within very narrow redox potential ranges [168]. This type of reactivity would be dependent on the oxidation state of the starting compound and may lead to different redox behavior along with different stereochemistry depending on whether the starting compound is in a lower or higher oxidation state.



## CHAPTER 3

### SYNTHESIS AND REACTIVITY OF THE COMPLEXES

#### EXPERIMENTAL

##### 3.1 Methods of Analysis and Work-up Manipulations

The elements carbon, hydrogen and nitrogen were analyzed by standard microanalytical techniques at Indian Institute of Technology, Kanpur. The procedures employed for the analysis of other elements are as follows:

##### Sulfur

About 0.3 g of the complex containing sulfur was treated with an excess of alkaline bromine water. The excess bromine was evaporated off by warming the solution slowly on a water bath. Hydrochloric acid was then added to the resulting solution and the liberated bromine was again evaporated off by

slow boiling of the solution. The solution was filtered and the sulfate in the filtrate was estimated by precipitating it as barium sulfate, in the usual manner [169].

#### Nickel and Palladium

Approximately 0.3 g of the compounds were decomposed by treating them with an excess amount of boiling aqua-regia. The resulting solution was evaporated to dryness. Treatment with aqua-regia and evaporation to dryness were carried out once more to ensure the total decomposition of the compound. The residue was treated with concentrated hydrochloric acid and the solution was evaporated to dryness. It was then dissolved in hot water and the solution was filtered. The metal in the filtrate was estimated gravimetrically as the dimethylglyoximate [169].

All the chemicals used were of analytical grade. The solvents were distilled prior to use. Manipulations to synthesize and isolate the air sensitive complexes were carried out under dinitrogen atmosphere. Only freshly prepared polysulfide solutions were used. These were prepared as follows:

#### Preparation of Aqueous Ammonium Polysulfide Solution

To a mixture of 40 g of finely crystalline sulfur and 100 ml of concentrated ammonia solution a moderately fast stream of hydrogen sulfide was passed with occasional stirring. The sulfur slowly dissolved and the solution became dark red

in color. Passing of hydrogen sulfide was continued for thirty minutes after the complete dissolution of sulfur. The impurities were then removed by rapidly filtering the solution under suction. The dark red solution of the polysulfide was stored in a tightly closed flask till the time of using [170].

#### Preparation of Potassium Polysulfide Solution in Dimethylformamide

A moderately fast stream of hydrogen sulfide was bubbled into a mixture of potassium hydroxide (4 g) and sulfur (20 g) in 100 ml of dimethylformamide for about two hours. The dark reddish brown solution was filtered to remove the unreacted sulfur and the polysulfide solution was kept in a tightly closed flask prior to use.

#### Preparation of Methanolic Potassium Polysulfide Solution

To a mixture of potassium hydroxide (4 g) and sulfur (20 g) in methanol (100 ml), a moderately rapid stream of hydrogen sulfide was passed for about two hours. The resulting orange-red solution was filtered to remove the excess sulfur and the polysulfide solution was stored in a tightly closed flask.

The compounds potassium tetracyanonickelate(II), tris-(1,10-phenanthroline)nickel(II) chloride, tris(2,2'-bipyridyl)nickel(II) chloride, potassium tetracyanopalladate(II),

dichloro(1,10-phenanthroline)palladium(II), dichloro(2,2'-bipyridyl)palladium(II), potassium tetracyanoplatinate(II) and carbonyl sulfide were prepared according to the literature methods [170-175].

### 3.2 Synthesis of Complexes Containing Only Polysulfide Ligands

#### 3.2(i) Preparation of $(PPh_4)_2[Ni(S_4)_2]$

Method A: 0.5 g of potassium tetracyanonickelate(II) monohydrate was added with stirring to 25 ml of freshly prepared ammonium polysulfide solution. The resulting solution was stirred in a stoppered flask for five minutes. The color of the solution became very dark brown. It was then filtered into a solution of 1.5 g of tetraphenylphosphonium chloride in 25 ml of methanol. Allowing the solution to stand for about thirty minutes gave reddish brown microcrystals. These were filtered, washed with little water, methanol, toluene (to remove the adhering sulfur impurities) and finally with diethyl ether. The product was dried under vacuum; yield ~40%.

Anal. Found: C, 58.40; H, 4.50; S, 25.60; Ni, 5.90%.

Calcd. for  $NiC_{48}H_{40}P_2S_8$ : C, 58.01; H, 4.03; S, 25.78; Ni, 5.94%.

Method B: 1.5 g of tetraphenylphosphonium chloride was dissolved in 50 ml of methanolic potassium polysulfide solution. 0.5 g of potassium tetracyanonickelate(II) dissolved in minimum

quantity of water was added to this solution with stirring. The resulting solution was boiled on a water bath for five minutes. When the color of the solution became very dark brown, the hot solution was quickly filtered under suction. The filtrate was allowed to stand in a stoppered flask at room temperature. In about an hour, dark brown crystals precipitated, which were filtered, washed with methanol, toluene and finally with diethyl ether. The compound was dried in a vacuum desiccator; yield  $\sim 40\%$ .

The analysis of this compound was identical to the one prepared from method A, described above.

### 3.2(ii) Preparation of $(\text{AsPh}_4)_2[\text{Ni}(\text{S}_4)_2]$

The procedure for the synthesis and isolation of this compound is similar to the one employed for  $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  except that tetraphenylarsonium chloride was used in place of tetraphenylphosphonium chloride. The compound was prepared by both the methods described above. The yields obtained were also similar.

Anal. Found: C, 53.82; H, 3.45; S, 23.81; Ni, 5.42%.

Calcd. for  $\text{NiC}_{48}\text{H}_{40}\text{As}_2\text{S}_8$ : C, 53.28; H, 3.70; S, 23.68; Ni, 5.46%.

### 3.2(iii) Preparation of $(Et_4N)_2[Ni(S_4)_2]$

1.0 g of tetraethylammonium bromide was dissolved in 50 ml of methanolic potassium polysulfide solution. 0.5 g of potassium tetracyanonickelate(II) was added to this solution in small portions with stirring. The resulting solution was boiled on a water bath for ten minutes and then quickly filtered. The filtrate was allowed to stand in a stoppered flask at 5°C. After several hours the precipitated, shining black crystals were filtered on a sintered crucible, washed with methanol, toluene, diethyl ether and dried under vacuum; yield ~30%.

Anal. Found: C, 33.42; H, 7.02; N, 5.21; S, 43.82; Ni, 10.72%. Calcd. for  $NiC_{16}H_{40}N_2S_8$ : C, 33.39; H, 6.96; N, 4.87; S, 44.52; Ni, 10.26%.

### 3.2(iv) Preparation of $(Et_4N)_2[PdS_{11}]$

2.0 g of tetraethylammonium bromide was dissolved in 30 ml of aqueous ammonium polysulfide solution. 1.0 g of potassium tetracyanopalladate(II) monohydrate was added to this solution with stirring. On keeping the solution for about half an hour, a red compound precipitated. It was filtered, washed with propanol, carbon disulfide, diethylether and then dried in a vacuum desiccator; yield ~80%.

Anal. Found: C, 26.20; H, 5.82; N, 3.95; S, 49.00; Pd, 14.62%. Calcd. for  $PdC_{16}H_{40}N_2S_{11}$ : C, 26.74; H, 5.57;

N, 3.90; S, 49.02; Pd, 14.76%.

### 3.2(v) Preparation of $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$

Method A: 1.0 g of potassium tetracyanopalladate(II) monohydrate was added with stirring to 100 ml ammonium polysulfide solution. The resulting dark orange solution was stirred at room temperature in a stoppered flask for two days. Addition of a solution of tetraethylammonium bromide (2.0 g) in water (30 ml) gave an orange yellow precipitate, which was filtered, washed with propanol, carbon disulfide, diethylether and dried under vacuum. The compound was recrystallized by dissolving it in minimum amount of dimethylformamide, filtering and adding diethylether. Allowing the solution to stand at room temperature gave beautiful orange-red crystals, which were filtered, washed thoroughly with carbon disulfide and diethylether. Dried in a vacuum desiccator; yield ~ 70%.

Anal. Found: C, 22.45; H, 4.90; N, 3.41; S, 56.28; Pd, 12.76%. Calcd. for  $\text{PdC}_{16}\text{H}_{40}\text{N}_2\text{S}_{15}$ : C, 22.70; H, 4.73; N, 3.31; S, 56.74; Pd, 12.53%.

Method B: 1.0 g of  $(\text{Et}_4\text{N})_2[\text{PdS}_{11}]$  was added in small portions with stirring to a solution of ammonium polysulfide (80 ml). A clear dark orange solution was obtained which on keeping for 2-3 days gave an orange-yellow precipitate. The product was isolated and purified as described in method A, above; yield ~ 70%.

The analysis of the compound prepared by this method was found to be identical to the one prepared from the above method A.

### 3.2(vi) Preparation of $(Et_4N)_2[Pd(S_4)_2]$

Method A: 10 ml of ammonium polysulfide solution prepared as described earlier, was diluted with 40 ml of concentrated ammonia solution. 0.5 g of potassium tetracyanopalladate(II) monohydrate was added with stirring and the solution was allowed to stand in a stoppered flask for two days. 1.0 g of tetraethylammonium bromide was added and on standing for a day, a very dark brown crystalline compound precipitated. It was filtered, washed with propanol, carbon disulfide, diethylether and dried in vacuum; yield ~ 40%.

Anal. Found: C, 30.69; H, 6.38; N, 4.81; S, 42.01; Pd, 16.96%. Calcd. for  $PdC_{16}H_{40}N_2S_8$ : C, 30.87; H, 6.43; N, 4.50; S, 41.16; Pd, 17.04%.

### Method B: Reaction of $[Pd(S_5)_3]^{2-}$ with $OH^-$

$(Et_4N)_2[Pd(S_5)_3]$ , (0.4 g) was dissolved in 20 ml of dimethylformamide and 10 ml of concentrated ammonia solution was added to it. On keeping the solution in a stoppered flask for two days the color changed from yellow to brown. Addition of little water gave a black-brown compound which was filtered, washed with propanol, carbon disulfide, diethylether and dried in a vacuum desiccator; yield ~ 20%.



The analysis of this compound was identical to the one obtained from the method A described above.

3.2(vii) Preparation of  $(\text{AsPh}_4)_2[\text{Pd}(\text{S}_4)_2]$ . (Reaction of  $[\text{Pd}(\text{S}_5)_3]^{2-}$  with  $\text{CN}^-$ )

$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$ , (0.3 g) was dissolved in 20 ml of dimethylformamide and a solution of potassium cyanide (0.12 g in 4 ml of  $\text{H}_2\text{O}$ ) was added to it dropwise with stirring. The color of the solution changed from yellow to brown. The stirring was continued for one hour and the resulting solution was filtered into a solution of tetraphenylarsonium chloride (0.3 g) in 50 ml of water. A brown compound separated immediately. It was filtered, washed with propanol, diethylether and dried under vacuum; yield  $\sim 70\%$ .

Anal. Found: C, 51.42; H, 3.82; S, 22.40; Pd, 9.13%.  
Calcd. for  $\text{PdC}_{48}\text{H}_{40}\text{As}_2\text{S}_8$ : C, 51.06; H, 3.55; S, 22.70; Pd, 9.40%.

3.2(viii) Preparation of  $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$

1.0 g of potassium tetracyanoplatinate(II) was added with stirring to 50 ml of ammonium polysulfide solution. The solution was stirred for ten minutes. Addition of a solution of tetraethylammonium bromide (2.0 g) in water (50 ml) gave a dark-red precipitate which was filtered, washed with propanol, carbon disulfide, diethylether and dried in a vacuum desiccator.

The compound was recrystallized by dissolving it in dimethylformamide, filtering the solution and adding diethylether to incipient crystallization and standing. The precipitated red crystals were filtered on a frit funnel, washed with carbon disulfide, diethylether and then dried under vacuum; yield  $\sim 70\%$ .

Anal. Found: C, 20.41; H, 4.15; N, 2.85; S, 51.51%.

Calcd. for  $\text{PtC}_{16}\text{H}_{40}\text{N}_2\text{S}_{15}$ : C, 20.53; H, 4.28; N, 2.99; S, 51.33%.

### 3.2(ix) Attempted Reaction of Nickel Dimethylglyoximate With polysulfide

0.5 g of bis(dimethylglyoximate)nickel(II) in 25 ml of methanol was added to 50 ml of methanolic potassium polysulfide solution. The solution was boiled on a water bath for ten minutes, 1.0 g of tetraphenylphosphonium chloride was added and filtered rapidly. The filtrate was allowed to stand at room temperature for a day, but, no precipitate was formed. Addition of water gave back the unreacted starting complex in almost quantitative yield.

### 3.2(x) Attempted Reaction of Tris(dimethylglyoximate)nickel(IV) With Polysulfide

To an aqueous solution of potassium tris(dimethylglyoximate)nickel(IV) (0.3 g in 25 ml) [176] was added a solution

of aqueous ammonium polysulfide (50 ml). Within five minutes of the addition bis(dimethylglyoximate)nickel(II) precipitated out and no nickel(IV) polysulfide complex could be isolated.

### 3.3 Synthesis of Complexes Containing Other Ligands in Addition to Polysulfide

#### 3.3(i) Preparation of $(PPh_4)_2[Ni(CN)_2(S_5)]$

0.65 g of potassium tetracyanonickelate(II) monohydrate, 0.8 g of sulfur and 0.3 g of finely powdered potassium hydroxide were taken in 50 ml of dimethylformamide. The mixture was stirred in a stoppered flask at room temperature for ten hours. The resulting dark brown solution was filtered and to the filtrate was added a solution of 1.8 g of tetraphenylphosphonium chloride in 10 ml of dimethylformamide. Any precipitate appearing at this stage was filtered off and to the filtrate 50 ml of diethylether was added. The solution on keeping in a refrigerator for two days gave dark greenish brown crystals. These were filtered, washed with propanol, toluene, diethylether and dried in a vacuum desiccator; yield ~ 20%.

Anal. Found: C, 63.62; H, 4.55; N, 3.26; S, 16.22; Ni, 6.08%. Calcd. for  $NiC_{50}H_{40}N_2P_2S_5$ : C, 63.22; H, 4.21; N, 2.95; S, 16.86; Ni, 6.22%.

#### 3.3(ii) Preparation of $(AsPh_4)_2[Ni(CN)_2(S_5)]$

The procedure for the preparation and isolation of this compound is similar to the one given above in 3.3(i) for

$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$  except that tetraphenylarsonium chloride was used in place of tetraphenylphosphonium chloride; yield ~20%.

Anal. Found: C, 57.52; H, 3.65; N, 3.07; S, 15.58; Ni, 5.45%. Calcd. for  $\text{NiC}_{50}\text{H}_{40}\text{N}_2\text{As}_2\text{S}_5$ : C, 57.86; H, 3.86; N, 2.70; S, 15.43; Ni, 5.69%.

### 3.3(iii) Preparation of $[\text{Ni}(\text{o-phen})(\text{S}_4)]$

1.0 g of tris(1,10-phenanthroline)nickel(II) chloride in 20 ml of methanol was added to a solution of methanolic potassium polysulfide (50 ml) with vigorous stirring. A violet-brown compound precipitated immediately which was filtered on a sintered crucible, washed with little water, methanol, toluene and diethylether. Dried in vacuum. Yield ~70%.

Anal. Found: C, 39.10; H, 2.06; N, 7.02; S, 34.62; Ni, 16.21%. Calcd. for  $\text{NiC}_{12}\text{H}_8\text{N}_2\text{S}_4$ : C, 39.24; H, 2.18; N, 7.63; S, 34.88; Ni, 16.08%.

### 3.3(iv) Preparation of $[\text{Ni}(\text{bipy})(\text{S}_4)]$

The procedure for the synthesis and isolation of this compound is similar to the one given above in 3.3(iii) for  $[\text{Ni}(\text{o-phen})(\text{S}_4)]$  except that tris(2,2'-bipyridyl)nickel(II)

chloride was used in place of tris(1,10-phenanthroline)-nickel(II) chloride. The yield of the violet-brown product was approximately 70%.

Anal. Found: C, 35.42; H, 2.81; N, 8.54; S, 37.02; Ni, 17.01%. Calcd. for  $\text{NiC}_{10}\text{H}_8\text{N}_2\text{S}_4$ : C, 34.99; H, 2.33; N, 8.16; S, 37.32; Ni, 17.20%.

### 3.3(v) Preparation of $[\text{Pd}(\text{o-phen})(\text{S}_4)]$

1.0 g of dichloro(1,10-phenanthroline)palladium(II) was added in small portions with stirring to 50 ml of potassium polysulfide solution in dimethylformamide. The mixture was stirred for an additional thirty minutes. The precipitated orange product was filtered, washed with little water, methanol, carbon disulfide and finally with diethylether. Dried in a vacuum desiccator; yield ~60%.

Anal. Found: C, 34.65; H, 1.82; N, 6.61; S, 30.97; Pd, 25.29%. Calcd. for  $\text{PdC}_{12}\text{H}_8\text{N}_2\text{S}_4$ : C, 34.78; H, 1.93; N, 6.76; S, 30.92; Pd, 25.60%.

This compound was also obtained when  $[\text{Pd}(\text{o-phen})\text{Cl}_2]$  was reacted with aqueous ammonium polysulfide.

### 3.3(vi) Preparation of $[\text{Pd}(\text{bipy})(\text{S}_4)]$

The procedure for the synthesis and isolation of this compound is similar to the one described above in 3.3(v) for

the preparation of  $[\text{Pd}(\text{o-phen})(\text{S}_4)]$  except that dichloro-(2,2'-bipyridyl)palladium(II) was used in place of dichloro-(1,10-phenanthroline)palladium(II). The yellow brown product was isolated in ~60% yield.

Anal. Found: C, 30.85; H, 2.45; N, 7.56; S, 32.02; Pd, 27.82%. Calcd. for  $\text{PdC}_{10}\text{H}_8\text{N}_2\text{S}_4$ : C, 30.77; H, 2.05; N, 7.18; S, 32.82; Pd, 27.18%.

### 3.4 Reaction of Polysulfido Complexes With Carbon Disulfide and Carbonyl Sulfide

#### 3.4(1) Reaction of $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$ with $\text{CS}_2$ . (Synthesis of $(\text{PPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$ )

To a solution of freshly prepared tetraphenylphosphonium bis(tetrasulfido)nickelate(II) (0.5 g) in 40 ml of dichloromethane, 10 ml of carbon disulfide was added. The solution was stirred for ten minutes and then filtered. Addition of diethylether to the filtrate gave yellowish brown crystals, which were filtered, thoroughly washed with diethylether and then dried under vacuum.

The compound was recrystallized by redissolving it in dichloromethane, filtering the solution, adding diethylether to incipient crystallization and standing; yield ~70%.

Anal. Found: C, 59.45; H, 3.80; S, 25.40; Ni, 5.72%. Calcd. for  $\text{NiC}_{50}\text{H}_{40}\text{P}_2\text{S}_8$ : C, 59.00; H, 3.93; S, 25.17; Ni, 5.80%.

3.4(ii) Reaction of  $(\text{AsPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with  $\text{CS}_2$ . (Synthesis of  $(\text{AsPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$ )

In a similar procedure described above in 3.9(i), this compound was prepared in about 70% yield.

Anal. Found: C, 54.81; H, 3.85; S, 23.05; Ni, 5.45%.  
Calcd. for  $\text{NiC}_{50}\text{H}_{40}\text{As}_2\text{S}_8$ : C, 54.30; H, 3.62; S, 23.17;  
Ni, 5.34 %.

3.4(iii) Reaction of  $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with COS. (Synthesis of  $(\text{PPh}_4)_2[\text{Ni}(\text{COS}_3)_2]$ )

A rapid stream of carbonyl sulfide was passed into a solution of freshly prepared tetraphenylphosphonium bis-(tetrasulfido)nickelate(II) (0.5 g) in 50 ml of dichloromethane for twenty minutes. The solution was filtered and the filtrate on addition of diethylether gave yellow-brown crystals. These were filtered, washed thoroughly with diethylether and then dried under vacuum. The compound was recrystallized from dichloromethane-ether; yield ~70%.

Anal. Found: C, 60.82; H, 3.92; S, 19.62; Ni, 5.82%.  
Calcd. for  $\text{NiC}_{50}\text{H}_{40}\text{O}_2\text{P}_2\text{S}_6$ : C, 60.91; H, 4.06; S, 19.49;  
Ni, 5.99%.

3.4(iv) Reaction of  $(\text{AsPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with COS. (Synthesis of  $(\text{AsPh}_4)_2[\text{Ni}(\text{COS}_3)_2]$ )

In a similar reaction to the one described above in 3.4(iii), this compound was prepared in about 70% yield.

Anal. Found: C, 55.60; H, 3.45; S, 18.28; Ni, 5.61%.  
 Calcd. for  $\text{NiC}_{50}\text{H}_{40}\text{O}_2\text{As}_2\text{S}_6$ : C, 55.92; H, 3.73; S, 17.89;  
 Ni, 5.50%.

3.4(v) Reaction of  $[\text{Ni}(\text{o-phen})(\text{S}_4)]$  with  $\text{CS}_2$ . (Synthesis of  $[\text{Ni}(\text{o-phen})(\text{CS}_4)]\cdot\text{DMF}$ )

1.0 g of freshly prepared tetrasulfido(1,10-phenanthroline)nickel(II) was added with stirring to a mixture of dimethylformamide (40 ml) and carbon disulfide (20 ml). The mixture on stirring for fifteen minutes gave a dark orange solution. This was filtered and to the filtrate 50 ml of methanol was added. Allowing the solution to stand for thirty minutes gave beautiful orange crystals, which were filtered, washed thoroughly with methanol, diethylether and dried in vacuum; yield ~80%.

Anal. Found: C, 42.43; H, 3.29; N, 9.10; S, 28.49; Ni, 12.78%. Calcd. for  $\text{NiC}_{16}\text{H}_{15}\text{N}_3\text{OS}_4$ : C, 42.48; H, 3.32; N, 9.29; S, 28.32; Ni, 13.05%.

3.4(vi) Reaction of  $[\text{Ni}(\text{bipy})(\text{S}_4)]$  with  $\text{CS}_2$ . (Synthesis of  $[\text{Ni}(\text{bipy})(\text{CS}_4)]$ )

This reaction was carried out in a similar manner described above in 3.4(v) using tetrasulfido(2,2'-bipyridyl)-nickel(II) and carbon disulfide in dimethylformamide. The red-orange crystals were isolated in ~80% yield.



Anal. Found: C, 37.32; H, 2.45; N, 7.59; S, 36.42; Ni, 16.24%. Calcd. for  $\text{NiC}_{11}\text{H}_8\text{N}_2\text{S}_4$ : C, 37.18; H, 2.25; N, 7.89; S, 36.06; Ni, 16.62%.

3.4(vii) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$  with  $\text{CS}_2$ . (Synthesis of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{CS}_4)_2]$ )

20 ml of carbon disulfide was added to a solution of 0.5 g of tetraethylammonium bis(tetrasulfido)palladate(II) in 30 ml of dimethylformamide. The solution was stirred for an hour and filtered. To the filtrate 50 ml of diethylether was added. After allowing the solution to stand at room temperature, the precipitated red-brown crystals were filtered, washed thoroughly with diethylether and dried in a vacuum desiccator; yield ~ 40%.

Anal. Found: C, 33.03; H, 6.15; N, 4.62; S, 39.92; Pd, 16.09%. Calcd. for  $\text{PdC}_{18}\text{H}_{40}\text{N}_2\text{S}_8$ : C, 33.44; H, 6.19; N, 4.33; S, 39.63; Pd, 16.41%.

3.4(viii) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$  with COS. (Synthesis of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{COS}_3)_2]$ )

0.5 g of tetraethylammonium bis(tetrasulfido)palladate(II) was added to 50 ml of dimethylformamide which was saturated with carbonyl sulfide. The passing of a rapid stream of carbonyl sulfide was continued for another thirty minutes. The solution was filtered and to the filtrate 70 ml

of ether was added. Allowing the solution to stand for a few hours at room temperature gave brown crystals, which were filtered, washed with diethylether and then dried under vacuum; yield ~40%.

Anal. Found: C, 35.34; H, 6.59; N, 4.72; S, 30.84; Pd, 17.10%. Calcd. for  $\text{PdC}_{18}\text{H}_{40}\text{N}_2\text{O}_2\text{S}_6$ : C, 35.18; H, 6.51; N, 4.56; S, 31.27; Pd, 17.26%.

#### 3.4(ix) Attempted Reaction of $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$ with $\text{CS}_2$

A similar reaction to the one given above in 3.4(vii) using tetraethylammonium tris(pentasulfido)palladate(IV) and carbon disulfide did not proceed to give the carbon disulfide inserted product and the starting complex was recovered in almost quantitative yield.

#### 3.4(x) Attempted Reaction of $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$ with $\text{CS}_2$

Reaction of tetraethylammonium tris(pentasulfido)-platinate(IV) with carbon disulfide carried out in a similar fashion as described earlier in 3.4(vii) did not give the carbon disulfide inserted product and the starting complex was recovered in near quantitative yield.

#### 3.4(xi) Attempted Reaction of $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$ with $\text{CO}_2$

A rapid stream of carbon dioxide was passed into 50 ml of dichloromethane for about thirty minutes. 0.5 g of freshly

prepared tetraphenylphosphonium bis(tetrasulfido)nickelate(II) was added and the passing of carbon dioxide was continued for another thirty minutes. A work-up similar to the one given above in 3.4(iii) gave a black residue which could not be characterized.

### 3.5 Reaction of Polysulfido Complexes With Substituted Acetylenes

#### 3.5(i) Reaction of $(PPh_4)_2[Ni(S_4)_2]$ with DBA. (Synthesis of $(PPh_4)[Ni(S_2C_2(COPh)_2)_2]$ )

0.5 g of freshly prepared tetraphenylphosphonium bis-(tetrasulfido)nickelate(II) and 0.25 g of dibenzoylacetylene (DBA) were taken in 50 ml of dichloromethane and stirred at room temperature for twenty minutes. The solution was filtered and to the filtrate an excess of diethylether was added. Keeping the solution in a refrigerator for a few hours gave dark red-brown microcrystals which were filtered and washed with ether. The product was recrystallized from dichloromethane-petroleum ether (40-60°C) mixture; yield ~50%.

Anal. Found: C, 67.09; H, 4.21; S, 12.52; Ni, 6.35%.  
Calcd. for  $NiC_{56}H_{40}O_4PS_4$ : C, 67.61; H, 4.02; S, 12.88; Ni, 5.94%.

3.5(ii) Reaction of  $(\text{AsPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with DBA. (Synthesis of  $(\text{AsPh}_4)[\text{Ni}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$ )

This reaction was carried out in a similar manner to the one described above in 3.5(i) and the dark brown product was isolated in about 50% yield.

Anal. Found: C, 64.06; H, 3.72; S, 12.01; Ni, 5.94%.

Calcd. for  $\text{NiC}_{56}\text{H}_{40}\text{O}_4\text{AsS}_4$ : C, 64.74; H, 3.85; S, 12.33; Ni, 5.68%.

3.5(iii) Reaction of  $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with DMAD. (Synthesis of  $(\text{PPh}_4)[\text{Ni}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]$ )

0.3 g of tetraphenylphosphonium bis(tetrasulfido)nickelate(II) and 0.1 ml of dimethylacetylenedicarboxylate (DMAD) were stirred in 50 ml of dichloromethane for twenty minutes. The solution was filtered and to the filtrate an excess of petroleum ether (40–60°C) was added. An oily mass separated. The supernatant liquid was decanted off and the oil was repeatedly washed with petroleum ether whereby it solidified. This was dissolved in dichloromethane filtered and petroleum ether was added till a turbidity appeared. Allowing the solution to stand for sometime gave brown crystals which were filtered, washed with petroleum ether and dried in a vacuum desiccator; yield ~ 25%.

Anal. Found: C, 53.05; H, 4.33; S, 15.55; Ni, 7.09%.

Calcd. for  $\text{NiC}_{36}\text{H}_{32}\text{O}_8\text{PS}_4$ : C, 53.33; H, 3.95; S, 15.80; Ni, 7.28%.

3.5(iv) Reaction of  $(\text{AsPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with DMAD. (Synthesis of  $(\text{AsPh}_4)[\text{Ni}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]$ )

In a similar procedure to the one described in 3.5(iii) above, this reaction gave the product in about 30% yield.

Anal. Found: C, 50.11; H, 3.55; S, 14.55; Ni, 6.70%.  
Calcd. for  $\text{NiC}_{36}\text{H}_{32}\text{O}_8\text{AsS}_4$ : C, 50.59; H, 3.75; S, 14.99; Ni, 6.91%.

3.5(v) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$  with DBA. (Synthesis of  $(\text{AsPh}_4)[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$ )

0.1 g of tetraethylammonium bis(tetrasulfido)palladate(II) and 0.15 g of dibenzoylacetylene were dissolved in 50 ml of dimethylformamide and the solution was heated on a water bath for one hour. 0.2 g of tetraphenylarsonium chloride was then added and the solution was filtered into 100 ml of water. A brown precipitate appeared immediately which was filtered, washed with methanol and diethylether. The product was dissolved in dichloromethane, filtered and to the filtrate petroleum ether (40-60°C) was added till a turbidity appeared. On standing, greenish brown microcrystals appeared, which were filtered, washed with diethylether and vacuum dried; yield ~ 50%.

Anal. Found: C, 62.64; H, 3.75; S, 11.25; Pd, 9.45%.  
Calcd. for  $\text{PdC}_{56}\text{H}_{40}\text{O}_4\text{AsS}_4$ : C, 61.94; H, 3.69; S, 11.80; Pd, 9.77%.

3.5(vi) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$  with DMAD. (Synthesis of  $(\text{AsPh}_4)[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]$ )

In a similar procedure to the one described above in 3.5(v), the reaction of tetraethylammonium bis(tetrasulfido)-palladate(II) and dimethylacetylenedicarboxylate in presence of tetraphenylarsonium chloride gave the green-brown micro-crystals in about 50% yield.

Anal. Found: C, 48.42; H, 3.72; S, 14.61; Pd, 11.29%.  
Calcd. for  $\text{PdC}_{36}\text{H}_{32}\text{O}_8\text{AsS}_4$ : C, 47.95; H, 3.55; S, 14.21; Pd, 11.76%.

3.5(vii) Reaction of  $(\text{Et}_4\text{N})_2[\text{PdS}_{11}]$  with DBA

This reaction was carried out by following a similar procedure as the one described in 3.5(v). The product obtained was identical to the one got from the reaction 3.5(v).

3.5(viii) Reaction of  $(\text{Et}_4\text{N})_2[\text{PdS}_{11}]$  with DMAD

This reaction was carried out in a similar procedure as given in 3.5(vi) and the same product was obtained.

3.5(ix) Reaction of  $[\text{Pd}(\text{o-phen})(\text{S}_4)]$  with DBA. (Synthesis of  $[\text{Pd}(\text{o-phen})(\text{S}_2\text{C}_2(\text{COPh})_2)]$ )

0.3 g of tetrasulfido(1,10-phenanthroline)palladium(II) and 0.3 g of dibenzoylacetylene were taken in 50 ml of

dimethylformamide and the suspension was heated on a water bath for eight hours. The orange-red solution was filtered and to the filtrate 20 ml of methanol was added. The precipitated orange-red solid was filtered on a sintered crucible, washed thoroughly with methanol, diethylether and dried under vacuum; yield ~20%.

Anal. Found: C, 57.20; H, 2.66; N, 4.62; S, 10.55; Pd, 18.30%. Calcd. for  $\text{PdC}_{28}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$ : C, 57.53; H, 3.08; N, 4.79; S, 10.96; Pd, 18.15%.

3.5(x) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$  with DBA. (Synthesis of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$ )

0.3 g of tetraethylammonium tris(pentasulfido)palladate(IV) and 0.4 g of dibenzoylacetylene were dissolved in 25 ml of dimethylformamide and the solution was heated on a water bath for two hours. The resulting solution was filtered and to the filtrate an excess of diethylether was added. On keeping the solution in a refrigerator, dark violet crystals precipitated in a few hours. These were filtered, washed with diethylether and dried in a vacuum desiccator; yield ~20%.

Anal. Found: C, 60.56; H, 5.72; N, 2.69; S, 15.81; Pd, 8.03%. Calcd. for  $\text{PdC}_{64}\text{H}_{70}\text{N}_2\text{O}_6\text{S}_6$ : C, 60.95; H, 5.56; N, 2.22; S, 15.20; Pd, 8.41%.

3.5(xi) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$  with DMAD. (Synthesis of  $(\text{AsPh}_4)_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$ )

0.1 g of tetraethylammonium tris(pentasulfido)palladate(IV) and 0.15 ml of dimethylacetylenedicarboxylate in 20 ml of dimethylformamide were heated on a water bath for two hours. 0.1 g of tetraphenylarsonium chloride was then added, the solution was filtered and to the filtrate an excess of diethylether was added. The precipitated brown residue was filtered, washed with methanol and diethylether. It was dissolved in dichloromethane, filtered and to the filtrate diethylether was added to initiate crystallization. After about half an hour the precipitated crystals were filtered, washed with diethylether and dried in a vacuum desiccator; yield ~ 50%.

Anal. Found: C, 53.85; H, 3.72; S, 12.44; Pd, 6.82%.  
Calcd. for  $\text{PdC}_{66}\text{H}_{50}\text{O}_{12}\text{As}_2\text{S}_6$ : C, 53.15; H, 3.89; S, 12.89; Pd, 7.11%.

3.5(xii) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$  with DBA. (Synthesis of  $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$ )

0.1 of tetraethylammonium tris(pentasulfido)platinate(IV) and 0.12 g of dibenzoylacetylene were dissolved in 25 ml of dimethylformamide and the solution was heated on a water bath for four hours. The resulting solution having a greenish tinge was filtered and to the filtrate an excess of methanol was added. On allowing the solution to stand overnight at room



temperature, red-brown needle shaped crystals precipitated. These were filtered, washed with methanol, diethylether and dried in vacuum; yield ~ 20%.

Anal. Found: C, 57.42; H, 4.83; N, 2.22; S, 14.46%.

Calcd. for  $\text{PtC}_{64}\text{H}_{70}\text{N}_2\text{O}_6\text{S}_6$ : C, 56.93; H, 5.19; N, 2.08; S, 14.23%.

3.5(xiii) Reaction of  $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$  with DMAD. (Synthesis of  $(\text{AsPh}_4)_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$ )

0.1 g of tetraethylammonium tris(pentasulfido)platinate(IV) and 0.12 ml of dimethylacetylenedicarboxylate in 25 ml of dimethylformamide were heated on a water bath for four hours. 0.1 g of tetraphenylarsonium chloride was added and the solution was filtered. To the filtrate an excess of diethylether was added. A brown solid precipitated, which was filtered, washed with methanol and diethylether. It was recrystallized from dichloromethane-diethylether; yield ~ 50%.

Anal. Found: C, 50.34; H, 3.53; S, 12.51%. Calcd. for  $\text{PtC}_{66}\text{H}_{58}\text{O}_{12}\text{As}_2\text{S}_6$ : C, 50.16; H, 3.67; S, 12.16%.

3.5(xiv) Attempted Reaction of  $(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$  with trans-stilbene

0.5 g of tetraphenylphosphonium bis(tetrasulfido)nickelate(II) and 0.3 g of trans-stilbene were dissolved in 40 ml of

dichloromethane and the solution was stirred for thirty minutes. It was filtered and the filtrate on addition of diethylether gave a black residue which could not be characterized.

### 3.6 Reaction of Polysulfido Complexes With Oxygen

#### 3.6(i) Preparation of $[\text{Ni}(\text{o-phen})(\text{S}_3\text{O}_2)]$

A solution of 1.0 g of tris(1,10-phenanthroline)nickel(II) chloride in 20 ml of water was added to a solution of 50 ml of aqueous ammonium polysulfide solution. A yellow-brown solid precipitated immediately. The mixture was stirred in presence of air for about one hour. It was filtered, washed with water, methanol, toluene and diethylether. Dried in vacuum; yield ~ 70%.

Anal. Found: C, 41.52; H, 2.20; N, 7.94; S, 24.07; Ni, 16.72%. Calcd. for  $\text{NiC}_{12}\text{H}_8\text{N}_2\text{O}_2\text{S}_3$ : C, 39.24; H, 2.18; N, 7.63; S, 26.15; Ni, 16.08%.

#### 3.6(ii) Preparation of $[\text{Ni}(\text{bipy})(\text{S}_3\text{O}_2)]$

The procedure employed for the synthesis and isolation of this compound was similar to the one given in 3.6(i) except that tris(2,2'-bipyridyl)nickel(II) chloride was taken instead of tris(1,10-phenanthroline)nickel(II) chloride; yield ~ 70%.

Anal. Found: C, 36.06; H, 2.21; N, 8.42; S, 26.09; Ni, 17.83%. Calcd. for  $\text{NiC}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}_3$ : C, 34.99; H, 2.33; N, 8.16; S, 27.99; Ni, 17.20%.

## RESULTS AND DISCUSSION

### 3.7 Synthetic Aspects and Bio-relevance of the Present Work

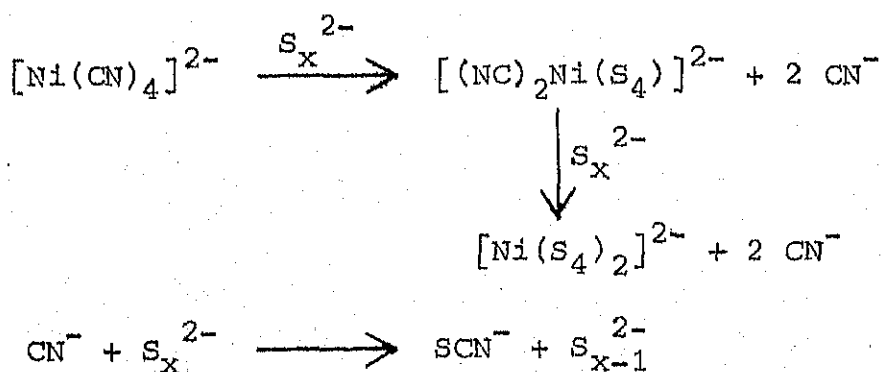
Tetracyanonickelate(II) anion is one of the most stable complexes of nickel (for example, nickel dimethylglyoximate is soluble in aqueous cyanide with the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$ ) and only very few substitution reactions of this complex anion are reported in the literature. Although many phosphine complexes of nickel cyanide are known, they are invariably made by addition to  $\text{Ni}(\text{CN})_2$  rather than by substitution in  $[\text{Ni}(\text{CN})_4]^{2-}$ . Yet, the following two observations prompted us to explore the reactivity of  $[\text{Ni}(\text{CN})_4]^{2-}$  with polysulfide.

(i) The very fast exchange between labelled cyanide and  $[\text{Ni}(\text{CN})_4]^{2-}$  in aqueous medium, involving the formation of  $[\text{Ni}(\text{CN})_5]^{3-}$  [175]; and

(ii) the curious cyanide elimination reaction by sulfide with the formation of  $[\text{Ni}(\text{CN})_3\text{S}]^{3-}$  [177]. The first observation implies that the coordination number in  $[\text{Ni}(\text{CN})_4]^{2-}$  can be easily enhanced and the second observation opens the possibility of cyanide elimination by sulfur donor ligands.

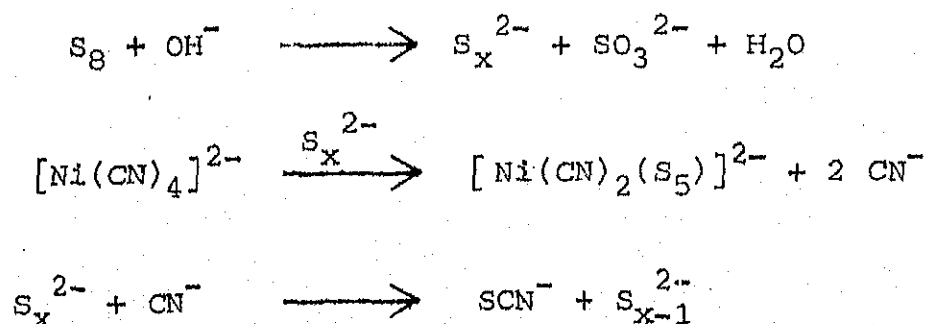
The reaction of  $[\text{Ni}(\text{CN})_4]^{2-}$  and polysulfide is quite facile both in aqueous and methanolic media. The color of the solution first becomes dark orange and then very dark brown within a very short time after the addition of the reagent.  $[\text{Ni}(\text{S}_4)_2]^{2-}$ , the complex anion formed can be easily isolated by using bulky cations. When this work was carried out [178], the synthesis of the same anion was also reported by Müller and coworkers by the reaction of nickel(II) acetate with methanolic ammonium polysulfide solution [43].

Probably the reaction proceeds by the stepwise replacement of cyanides by polysulfide ligand with the intermediate formation of a dicyano(tetrasulfido)nickel(II) species. The cyanides will be converted into thiocyanate as soon as they get replaced, by reaction with the sulfur of polysulfide and hence, the reversibility of the reaction would be easily checked. The proposed tentative scheme is as follows:



The proposal for the formation of the dicyano(tetrasulfido)-nickel(II) intermediate seems reasonable in the light of the

isolation of  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  by the reaction of  $[\text{Ni}(\text{CN})_4]^{2-}$  with sulfur and potassium hydroxide in dimethylformamide. The difference in isolating the cyano substituted complex over the bis(tetrasulfido)nickelate(II) anion lies in changing the solvent system as well as the concentration of the polysulfide. In any polysulfide solution the concentration of  $\text{S}_5^{2-}$  is predominant in nature. In the aqueous medium with high concentration of the polysulfide the reaction is very fast and the complete substitution process takes place. However, the generation of the  $\text{S}_x^{2-}$  in the reaction medium in a controlled manner by the use of sulfur and KOH in DMF leads to the formation of the cyanosubstituted product. Curiously the ring size is  $\text{NiS}_5$  and the extra stability could be due to the presence of the coligand (vide infra). It is difficult to pinpoint the mechanistic aspect of this reaction. The possible course of the reaction could be as follows:



The reaction of  $[\text{Pd}(\text{CN})_4]^{2-}$  with aqueous polysulfide is also interesting since depending on the reaction conditions different compounds can be obtained. When short reaction time

and moderately excess of polysulfide solution are used the reaction readily yields the well-known  $[\text{PdS}_{11}]^{2-}$  in high yield. But with large excess of polysulfide and over a long period of time, the palladium(IV) complex  $[\text{Pd}(\text{S}_5)_3]^{2-}$  is formed which can be isolated as tetraethylammonium salt. Presumably  $[\text{PdS}_{11}]^{2-}$  is formed first in the reaction medium which then slowly gets oxidized by polysulfide or sulfur radical anion which would be present in polar polysulfide solution, to form the palladium(IV) compound. This can be seen by the fact that  $[\text{PdS}_{11}]^{2-}$  readily dissolves in polysulfide solution and over a period of time gives the palladium(IV) compound. The oxidation of Pd(II) to Pd(IV), even though novel, is not very surprising, since the corresponding Pt(IV) compound can also be prepared by a polysulfide oxidation of the Pt(II) compound [56]. Oxidation of Pd(II) to Pd(IV) by a sulfur radical ion in DMF medium during the reaction of  $[\text{PdS}_{11}]^{2-}$  with cyanide is also reported [58].

All attempts to isolate the complex anion  $[\text{Pd}(\text{S}_5)_3]^{2-}$  as its ammonium or potassium salt are unsuccessful. In the absence of tetraethylammonium, always only the  $[\text{PdS}_{11}]^{2-}$  is precipitated as its ammonium salt. The insolubility of this compound precludes the palladium system to react further with polysulfide for the said oxidation process.

Nucleophilic degradation of  $[\text{Pd}(\text{S}_5)_3]^{2-}$  using cyanide and hydroxide lead to the formation of  $[\text{Pd}(\text{S}_4)_2]^{2-}$ . The

desulfurization reaction in this case is interesting for two reasons:

- (i) The reduction of Pd(IV) to Pd(II) which is the reverse of the reaction reported by Krause and coworkers in DMF medium [58]; and
- (ii) the isolation of bis(tetrasulfido)palladium(II) instead of bis(pentasulfido)palladium(II) analogous to platinum reactions [56].

When excess of cyanide is used all the polysulfide ligands get substituted by cyanides. So it can be easily visualized that the species present in a solution containing palladium, polysulfide and cyanide depend on the relative concentrations of polysulfide and cyanide.

It is known that the reaction of polysulfide with metal complexes is highly sensitive to the reaction conditions such as the concentration of polysulfide, the solvents used and the counter ions employed for the isolation of complex ions (cf. Chapter 1). The reactions of  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Pd}(\text{CN})_4]^{2-}$  with polysulfide, discussed above amply corroborate this fact. We have isolated two and three products in the case of nickel and palladium, respectively, by slight variations in the reaction conditions.

The reaction of  $[\text{Pt}(\text{CN})_4]^{2-}$  with aqueous polysulfide gives, as expected, the well known  $[\text{Pt}(\text{S}_5)_3]^{2-}$ . Here also

the polysulfide acts as an oxidizing agent.

In an attempt to synthesize the nickel(IV) analog of the palladium and platinum polysulfide complexes, the reaction of the nickel(IV) complex  $[\text{Ni}(\text{DMG})_3]^{2-}$  with polysulfide was tried in aqueous medium. The polysulfide solution in this case could not stabilize the nickel(IV) complex and slowly the nickel(II) dimethylglyoximate precipitated out from the solution. However, failure of this reaction does not preclude the possibility to stabilize the nickel(IV) with polysulfide ligand. We feel that a suitable reaction medium along with the use of other tetravalent nickel compounds may produce the desired nickel(IV) complex.

Reactions of octahedral nickel(II) complexes  $[\text{Ni}(\text{o-phen})_3]\text{Cl}_2$  and  $[\text{Ni}(\text{bipy})_3]\text{Cl}_2$  with polysulfide did not give the expected octahedral complexes containing polysulfide ligand, instead, square-planar complexes of the formulae  $[\text{Ni}(\text{o-phen})(\text{S}_4)]$  and  $[\text{Ni}(\text{bipy})(\text{S}_4)]$  are obtained, respectively (vide infra). The analogous  $[\text{Pd}(\text{o-phen})(\text{S}_4)]$  and  $[\text{Pd}(\text{bipy})(\text{S}_4)]$  are also prepared by the reaction of  $[\text{Pd}(\text{o-phen})\text{Cl}_2]$  and  $[\text{Pd}(\text{bipy})\text{Cl}_2]$  in DMF with potassium polysulfide, respectively. Square-planar complexes obtained in the case of palladium are as expected. For nickel system it appears that  $\text{S}_4^{2-}$  is very strong as a ligand. However, the strength of  $\text{S}_4^{2-}$  is not greater than the aromatic diimines, yet, sulfur donor ligands have some other exclusive properties which dictate square-planar stereochemistry (vide infra).



The tetrasulfido complexes described earlier, react with carbon disulfide in a very facile manner giving the perthio-carbonato complexes. The reaction of  $[\text{Ni}(\text{S}_4)_2]^{2-}$  with  $\text{CS}_2$  in dichloromethane to form  $[\text{Ni}(\text{CS}_4)_2]^{2-}$  is very fast and the complex anion can be easily isolated by employing bulky counter cations. Coucouvanis et al. have reported the synthesis of this complex anion by the reaction of  $[\text{Ni}(\text{CS}_3)_2]^{2-}$  with elemental sulfur [179-180]. Till date, there is only one other example of this kind of  $\text{CS}_2$  insertion in a polysulfido complex [131]. The corresponding  $[\text{Pd}(\text{CS}_4)_2]^{2-}$  is also prepared by the reaction of  $[\text{Pd}(\text{S}_4)_2]^{2-}$  with  $\text{CS}_2$  in an analogous manner.  $[\text{Ni}(\text{o-phen})(\text{S}_4)]$  and  $[\text{Ni}(\text{bipy})(\text{S}_4)]$  also react with  $\text{CS}_2$  in a facile manner to give the corresponding perthiocarbonato complexes. The reactions of  $[\text{Pd}(\text{S}_5)_3]^{2-}$  and  $[\text{Pt}(\text{S}_5)_3]^{2-}$  with  $\text{CS}_2$ , however, did not give the corresponding perthiocarbonato complexes and the starting materials are recovered in almost quantitative yield. The stability of  $\text{MS}_5$  ring is presumably high when the metal ion is in a higher oxidation state. Furthermore, the stereochemistry of these compounds is hexa-coordinate having spin paired  $d^6$  system. These two factors may be contributing towards the unreactivity of these complexes with  $\text{CS}_2$ .

Coucouvanis and Draganjac have forwarded two tentative mechanisms for the formation of  $\text{CS}_4^{2-}$  ligands in the reaction of tetrasulfido complexes with  $\text{CS}_2$  [131]. The first one proposes an electrophilic attack by  $\text{CS}_2$  on the coordinated

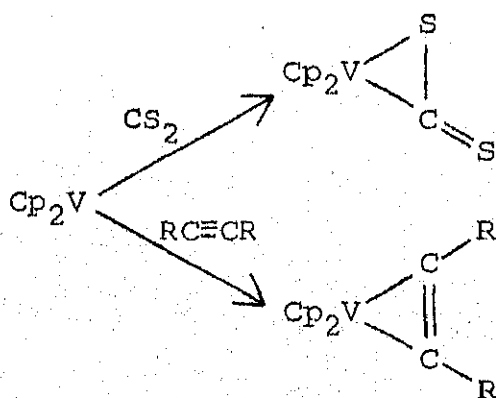
$S_4^{2-}$  ligands, subsequent rearrangement and elimination of elemental sulfur. The second mechanism proposes the dissociation of a  $S_2$  unit from the coordinated  $S_4^{2-}$  with the formation of a highly reactive metal-disulfide ( $M \begin{smallmatrix} S \\ | \\ S \end{smallmatrix}$ ) unit, which could be susceptible to electrophilic attack by  $CS_2$  on one of the two sulfur atoms of the disulfide ligand and then insertion into the Mo-S bond and rearrangement, or by a cycloaddition reaction. We have noticed that  $CS_4^{2-}$  formation in the reaction of nickel polysulfide complexes with  $CS_2$  is very facile which can be seen even by washing the solid polysulfido complexes repeatedly with carbon disulfide. Also the  $MS_4$  ring in these complexes is not very stable and in solution invariably it starts decomposing. This observation suggests that of the two proposed mechanisms the second one may be operative in these cases.

The insertion reactions are also found to proceed with carbonyl sulfide in a similar manner and the corresponding  $COS_3^{2-}$  complexes are isolated in fairly high yields. The reaction of  $[Ni(S_4)_2]^{2-}$  with carbon dioxide, however, did not give any insertion product.

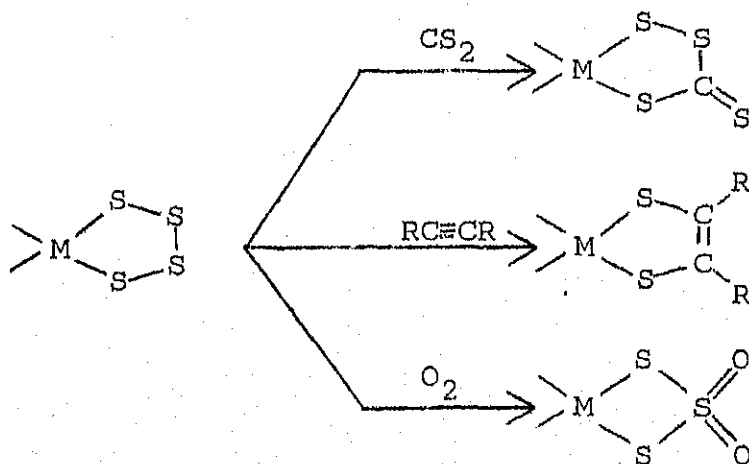
Another interesting aspect of the coordinated polysulfides is their reactions with substituted acetylenes with the formation of dithiolene complexes. The mechanistic aspect of this type of reaction also cannot be said with certainty. Here also, there can be a dissociative mechanism by which an in situ

generated  $MS_2$  fragment can then interact with the acetylene to produce the dithiolene moiety or an associative mechanism where the acetylene can attach to a metal bound sulfur atom with the formation of a dipolar intermediate. Interestingly when bis-(tetrasulfido) complexes are used the corresponding bis(dithiolene) complexes are formed where the central metal ion has been oxidized by one unit. The oxidizing agent here could be the sulfur formed as byproduct in this type of reaction. However, when a substituted tetrasulfido complex  $[Pd(o\text{-phen})(S_4)]$  is taken, the corresponding dithiolene complex can be isolated in the same oxidation state. The tris(pentasulfido) complexes of Pd(IV) and Pt(IV) react identically with the formation of the corresponding tris(dithiolene) complexes in the +4 oxidation state. The type of reactions described here are similar to those reported for some other polysulfide coordinated complexes [123].

The reactivity of tetrasulfido complexes with  $CS_2$  and  $RC\equiv CR$  may be comparable to that found in some organometallic complexes like  $Cp_2V$  as shown below [181].



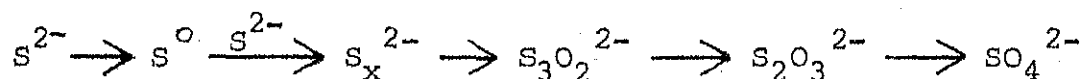
Yet another interesting aspect of the polysulfide coordinated complexes of nickel is their reactivity towards molecular oxygen. Fixation of the dithiosulfate ion,  $S_3O_2^{2-}$  has been recently reported in a molybdenum system [112]. We have noticed that the tetrasulfido complexes of nickel described earlier are very susceptible to oxygen especially in solution and it is practically impossible to do any solution measurements of these complexes (vide infra). In aerated medium synthesis of complexes of the type  $[Ni(L-L)(S_3O_2)]$  ( $L-L =$  o-phen or bipy) has been made. We have been unable to recrystallize these compounds, however, their spectral data (vide infra) indicate the presence of  $S_3O_2^{2-}$  group. Thus, the reactivity of  $MS_4$  ring with species like  $O_2$ ,  $CS_2$  and  $RC\equiv CR$  can be summarized as shown below:



### Bio-relevance

The bioinorganic aspect of nickel is emerging contemporarily. Besides the role of nickel in human system in the form of nickeloplasmin [182], recently it joined the group of transition metals relevant in biological oxidation-reduction processes. Hydrogenases have been long recognized as iron-sulfur clusters. Albracht et al. [183] first reported that Chromatium hydrogenase which is a single  $\text{Fe}_4\text{S}_4$  cubane type cluster is esr silent in both its oxidized and reduced states. They proposed that a second paramagnetic species, probably nickel is interacting with the iron system to make it esr silent. The presence of nickel as Ni(III) (esr active) has been demonstrated in several hydrogenases. The hydrogenase activity of the Chromatium enzyme depends on the presence of nickel in the growth medium. It has also been detected in the purified D. desulfuricans and D. gigas hydrogenases [184,185] and has been found essential for the chemolithotropic growth of free-living Rhizobium japonicum and its expression of hydrogenase [186]. Methanobacterium thermoautotrophicum not only requires nickel for the biosynthesis of hydrogenase, but produces an enzyme in which Ni(III) is the only esr active redox sensitive component [187]. However, the ligational aspect of this nickel center is not known. The interesting aspect of this finding lies in the appearance of rhombic esr signal. It is important to note that the formation of bis(dithiolene)-nickel(III) complexes by simply treating the starting

can combine to give  $S_x^{2-}$ ) the sulfur rich ion  $S_2O_3^{2-}$  may not be the only intermediate [188,189] and the involvement of previously undetected-species like  $S_3O_2^{2-}$  in the following way is quite possible.



It is known that in hydrothermal or very polluted water anoxic sediment or in flooded soil intermediate oxidation states of sulfur containing systems like polysulfides, thiosulfates, thionates and sulfites may occur [164]. Thus, the several other metastable sulfur species yet uncharacterized may be present in this oxidative part of the sulfur cycle, the use of these is an exclusive privilege of the biosphere.

## CHAPTER 4

### STRUCTURAL ASPECTS OF THE SYNTHESIZED COMPLEXES

#### EXPERIMENTAL

##### Electronic Spectra

Electronic spectra were recorded on Cary-17D and Shimadzu UV-190 double beam spectrophotometers using matched quartz cells. For solid state spectra samples were prepared as KBr pellets.

##### Vibrational Spectra

Infrared spectra of the samples were recorded on a Perkin Elmer Model-580 infrared grating spectrophotometer. Samples were prepared as CsI pellets.

Raman spectrum of  $(Et_4N)_2[Pd(S_5)_3]$  was recorded on a Spex-1403 Ramalog spectrophotometer using 514.5 nm line from

165 Argon ion laser. The sample was prepared as KBr pellet. A rotating cell was used to prevent decomposition of the compound. The spectrophotometer was calibrated using carbon tetrachloride.

#### Magnetic Susceptibility and ESR Spectra

Magnetic susceptibility measurements were carried out on an EG and G Model-150A parallel field vibrating sample magnetometer.

Electron spin resonance spectra were obtained on a Varian E-109 EPR system working at X-band.

#### X-Ray Photoelectron Spectrum

The XPS measurements of  $(PPh_4)_2[Ni(CN)_2(S_5)]$  were performed on an AEI ES200 electron spectrometer. The compound was mechanically spread out as a thin film on a platinum foil.  $AlK_{\alpha}$ -radiation (1486.6 eV) was used. The binding energies were calibrated to  $C_{1s} = 285.5$  eV of the  $PPh_4^+$  ion.

#### Electrochemical Studies

Electrochemical studies were performed with a three electrode system and a PAR Model-173 potentiostat, Model-174 polarographic analyzer and Model-775 signal generator. A Beckman platinum inlay electrode was used as working electrode for cyclic voltammetry and dropping mercury electrode for differential pulse polarography. All potentials were measured



versus a saturated calomel electrode. Potential measurements have a precision of  $\pm 0.005$  V.

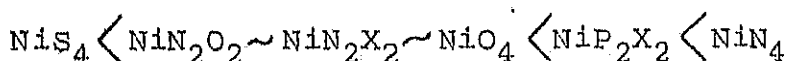
## RESULTS AND DISCUSSION

### 4.1 Electronic Spectra

Most of the complexes described in this thesis contain ligands with sulfur donors. The nickel species is spectroscopically interesting because of the large number of stereochemical forms in which the metal ion can be stabilized. Six coordinated octahedral nickel(II) complexes show a simple spectrum involving the transitions to the  ${}^3T_{2g}$ ,  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  levels, where the ground level is  ${}^3A_{2g}$ . When the six coordinate metal(II) complexes are having lower symmetry, the  $\nu_1$  band ( ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ) often splits into two components. For tetragonally distorted complexes, if the energy separation between  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals is sufficiently large to occur spin pairing, then diamagnetic six coordinate tetragonal complexes are produced. The distinction between this type of complex and a regular square complex is difficult to make spectroscopically. In some compounds temperature dependent spectra of borderline case has indicated spin paired and spin free behavior [190]. For the tetrahedral geometry three transitions from  ${}^3T_1$  ground state to  ${}^3T_2$ ,  ${}^3A_2$  and  ${}^3T_1(P)$  are expected in the visible region. The third transition can be readily characterized with high intensity and the second one

comes near near-infrared region having intensity higher than the octahedral complexes. However, solution spectra are difficult to interpret between these two geometries because there is every chance of having an equilibrium between tetrahedral and octahedral forms which cannot be distinguished even from solution magnetic studies.

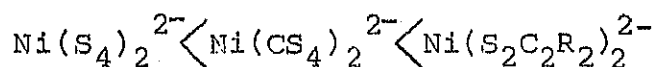
Elemental analysis and other studies (vide infra) suggest that the divalent complexes described here are all four coordinate. Thus, the available chromophores are  $\text{NiS}_4$ ,  $\text{NiC}_2\text{S}_2$ ,  $\text{NiN}_2\text{S}_2$  and for palladium,  $\text{PdS}_4$  and  $\text{PdS}_2\text{N}_2$ . In the mixed ligand complexes, cyanide or aromatic diimines are used which fall in the strongest part of the spectrochemical series. In the case of pure sulfur chromophore, normally it is observed that the lowest energy band which is responsible for the transition  $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$  lies in the lowest energy with respect to other chromophoric groups as shown below [191]:



The square-planar geometries of these complexes have been confirmed by their diamagnetic nature and thus, these general observations of the low value of  $10\text{Dq}$  (transition from  $d_{xy} \rightarrow d_{x^2-y^2}$ ) apparently contradicts the generalization that the square coordination is favoured by strong field ligands. It is generally believed that the nephelauxetic effect of sulfur could greatly reduce the pairing energy. In other

words, significant covalency in the metal-ligand  $\pi$  and  $\sigma$  bonds arise. This is particularly important for the out-of-plane  $\pi$ -bonding which promotes the  $\pi^*$  ( $b_{2g}$  or  $b_{3g}$ ) and  $\pi^*$  ( $a_g$ ) orbitals close to  $\sigma^*$  ( $b_{1g}$ ) and in the case of dithiolene complexes these energy differences are even closer than those in  $[M(CN)_4]^{2-}$  complexes [192-194]. The overall effect of these modified interactions could then account for the relatively small transition energies observed in these complexes.

A pictorial representation of the possible mode of  $\pi$ -interaction between the sulfur donor ligands with the out of plane  $\pi$ -d orbital ( $d_{xz}$ ) is shown in Fig. 4.1.1. Thus, if this  $\pi$ -delocalization is a major factor for stabilizing these complexes in square-planar coordination, then stability of the following order:



is expected. For the dithiolene ligands a complete delocalization in the ring would favor the maximum stability. In the  $S_4^{2-}$  coordinated complex the X-ray structural study [43] indicates a spirobicycle arrangement where the  $\pi$ -delocalization within  $NiS_4$  ring is severely hindered causing least stability of this anion. To augment the stability, the facile conversion of coordinated  $S_4^{2-}$  group to  $CS_4^{2-}$  is achieved simply by reacting the compound with carbon disulfide. The

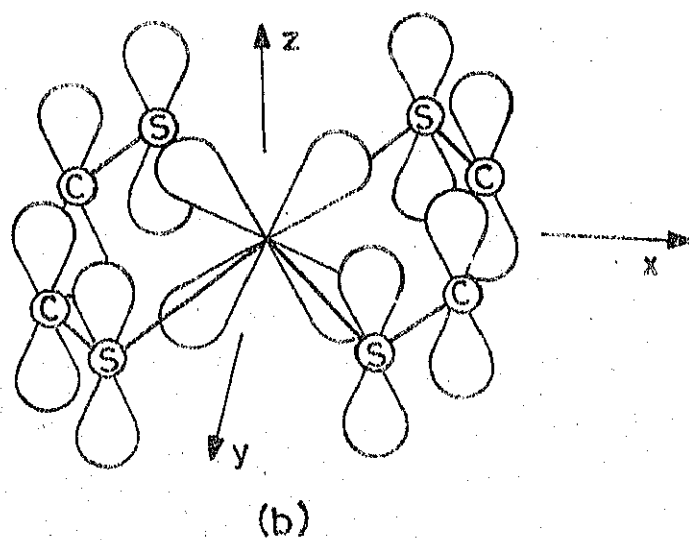
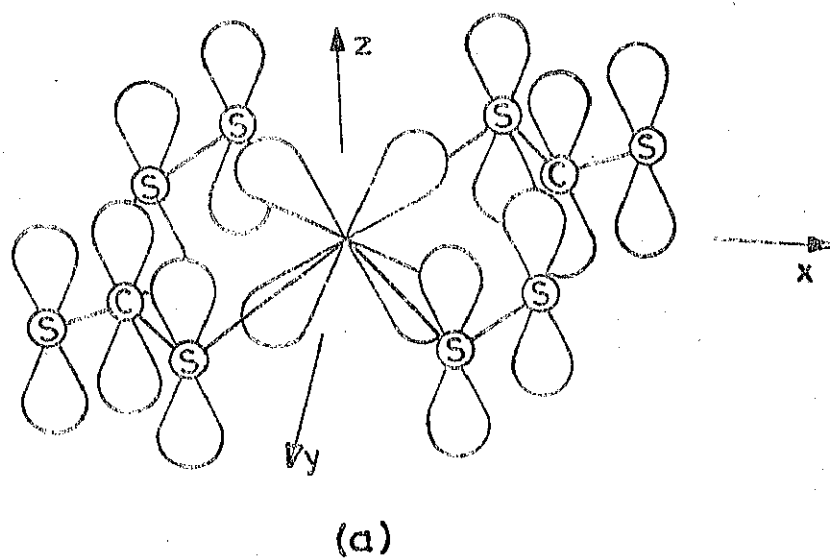
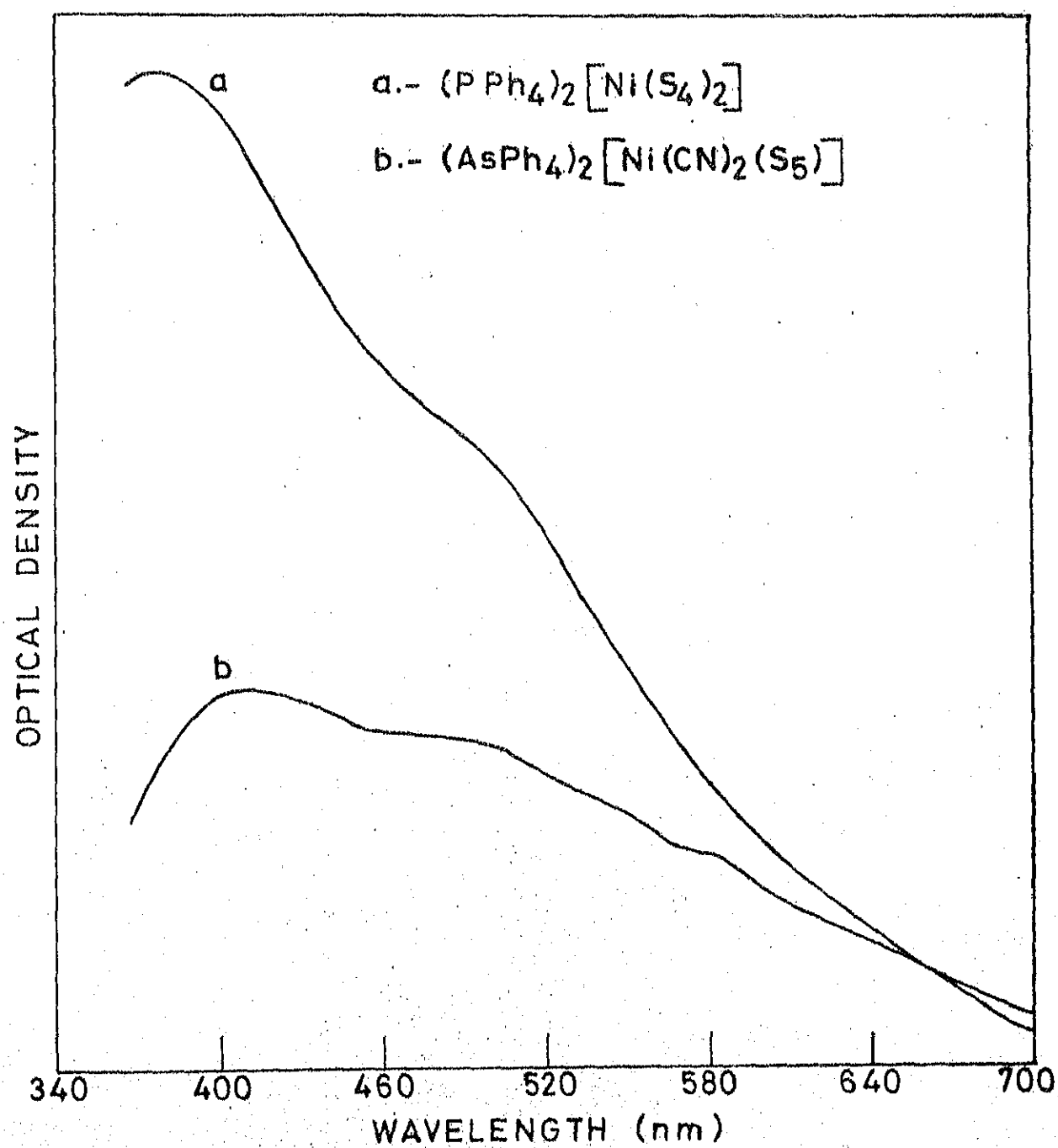


FIG. 4.1.1 OUT OF PLANE  $\pi$ -d ORBITAL OF THE  
 (a) NICKEL-PERTHIOCARBONATE AND  
 (b) NICKEL-DITHIOLENE SYSTEMS.

planarity of this coordinated  $\text{CS}_4^{2-}$  contributes to the stability of  $[\text{Ni}(\text{CS}_4)_2]^{2-}$ .

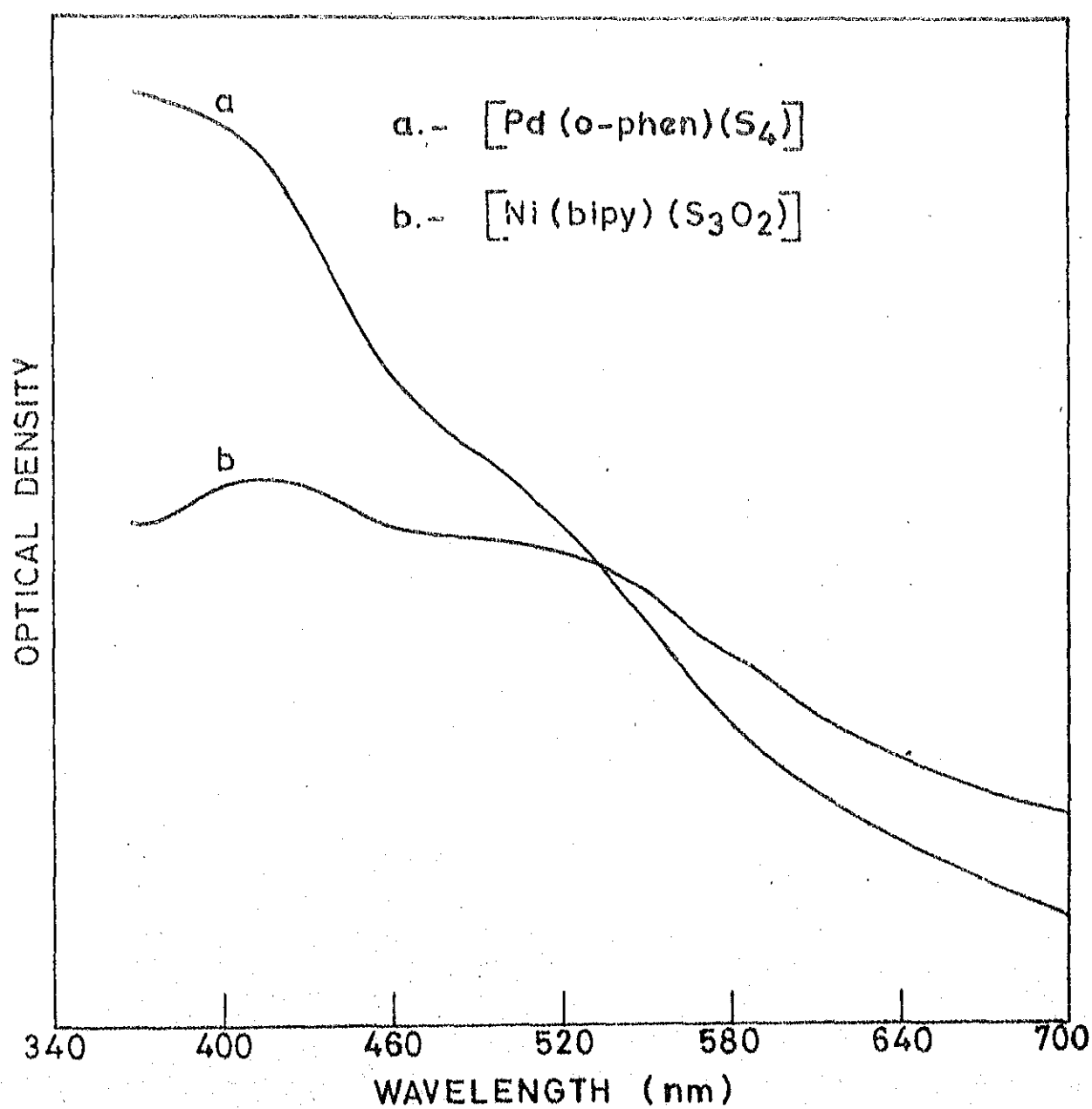
For square-planar nickel(II), the two major bands can be assigned to the  $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$  ( $b_{2g} \rightarrow b_{1g}$ ) and  $^1\text{B}_{1g} \rightarrow ^1\text{A}_{1g}$  ( $a_{1g} \rightarrow b_{1g}$ ) [195]. When  $\pi$ -bonding interactions are taking place the  $e_g$  orbitals become dissimilar in energy from the  $b_{2g}$  and  $a_{1g}$  orbitals and extra bands are observed. The problem is further complicated in that, the position of the  $a_{1g}$  ( $d_{z^2}$ ) orbital changes when the molecule deviates from truly square-planar nature with no near neighbours along the z-axis. Furthermore, the  $\pi$ -interaction makes the molar absorption values quite high. Thus, a proper distinction between a charge transfer transition and a d-d transition cannot be done so readily. When the corresponding palladium systems are used a similar trend is observed and all the transitions are shifted to higher energy side of the spectrum. For the substituted compounds  $[\text{Ni}(\text{CN})_2\text{S}_5]^{2-}$ , and  $[\text{Ni}(\text{L-L})(\text{S}_3\text{O}_2)]$  (L-L = o-phen, bipy) the stability precludes the recording of solution electronic spectra, like for  $[\text{Ni}(\text{S}_4)_2]^{2-}$ . The solid state spectra of these species are reproduced along with the spectra of the species described above in Figs. 4.1.2 - 4.1.6. The band maxima of all these species are tabulated in Tables 4.1.1 and 4.1.2.

The solid state spectrum of  $[\text{Ni}(\text{S}_4)_2]^{2-}$  agrees well with that reported by Müller and coworkers [43], prepared by a



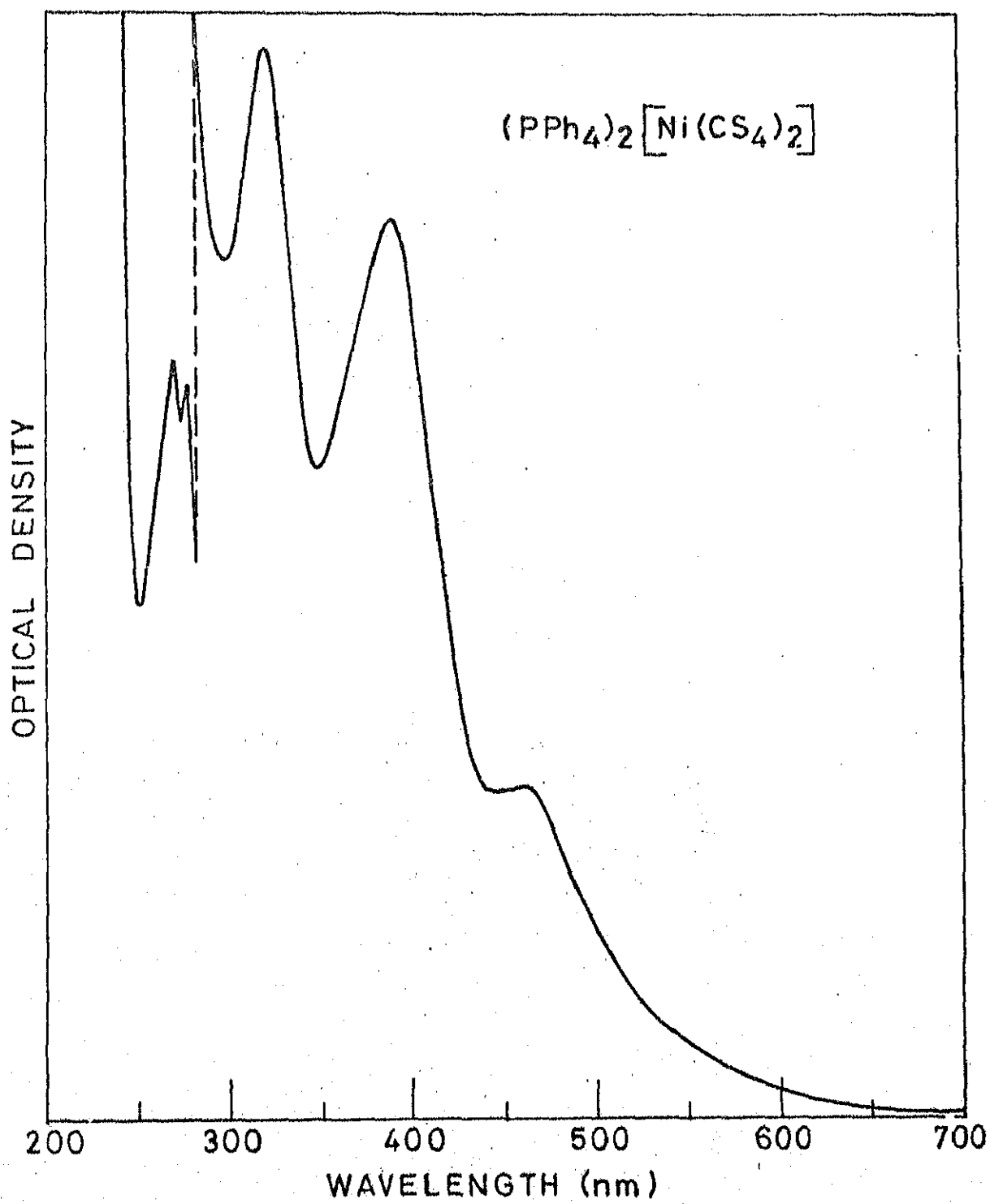
SOLID STATE ELECTRONIC SPECTRA

FIG. 4.1.2



SOLID STATE ELECTRONIC SPECTRA

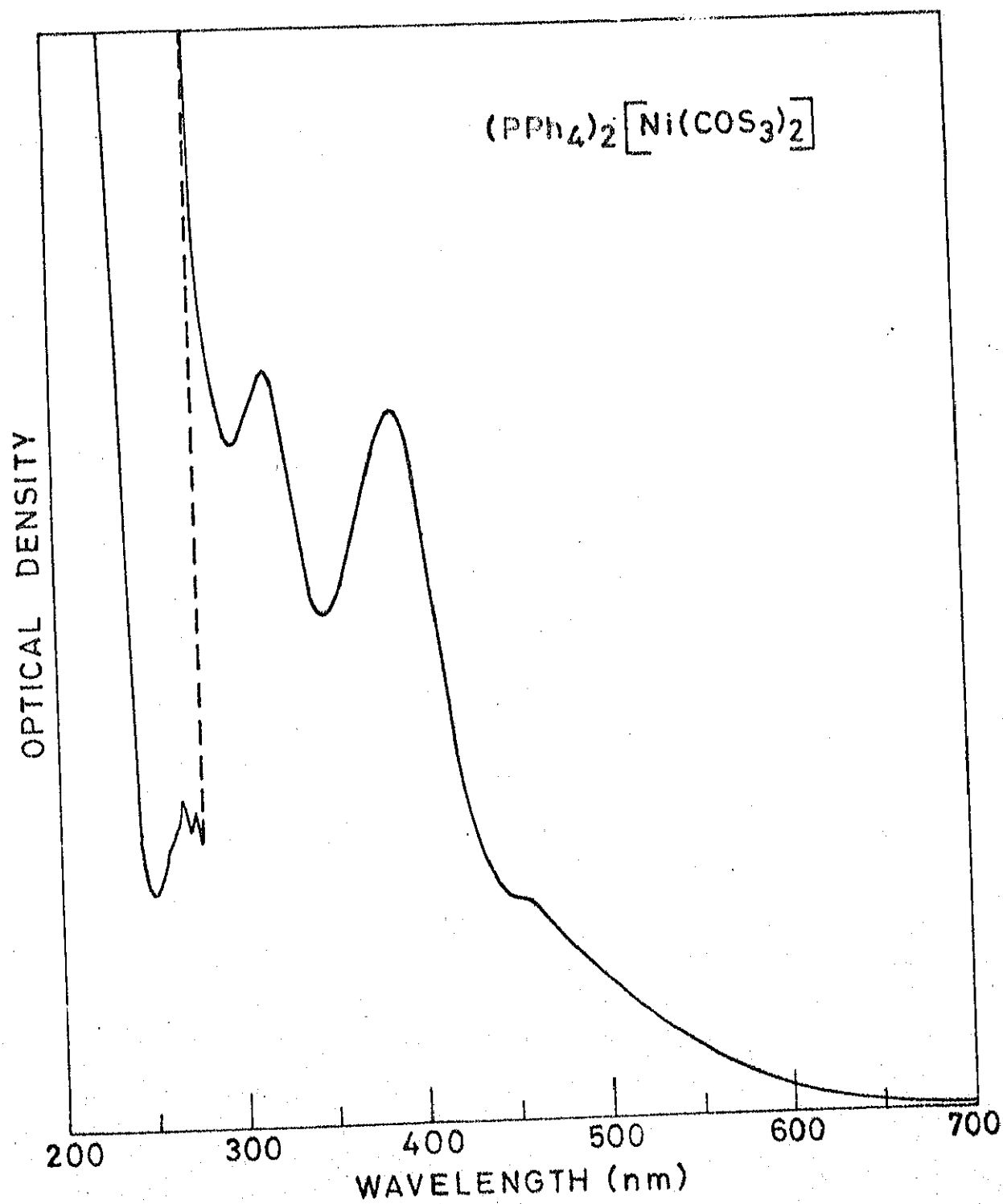
FIG. 4.1.3



ELECTRONIC SPECTRUM

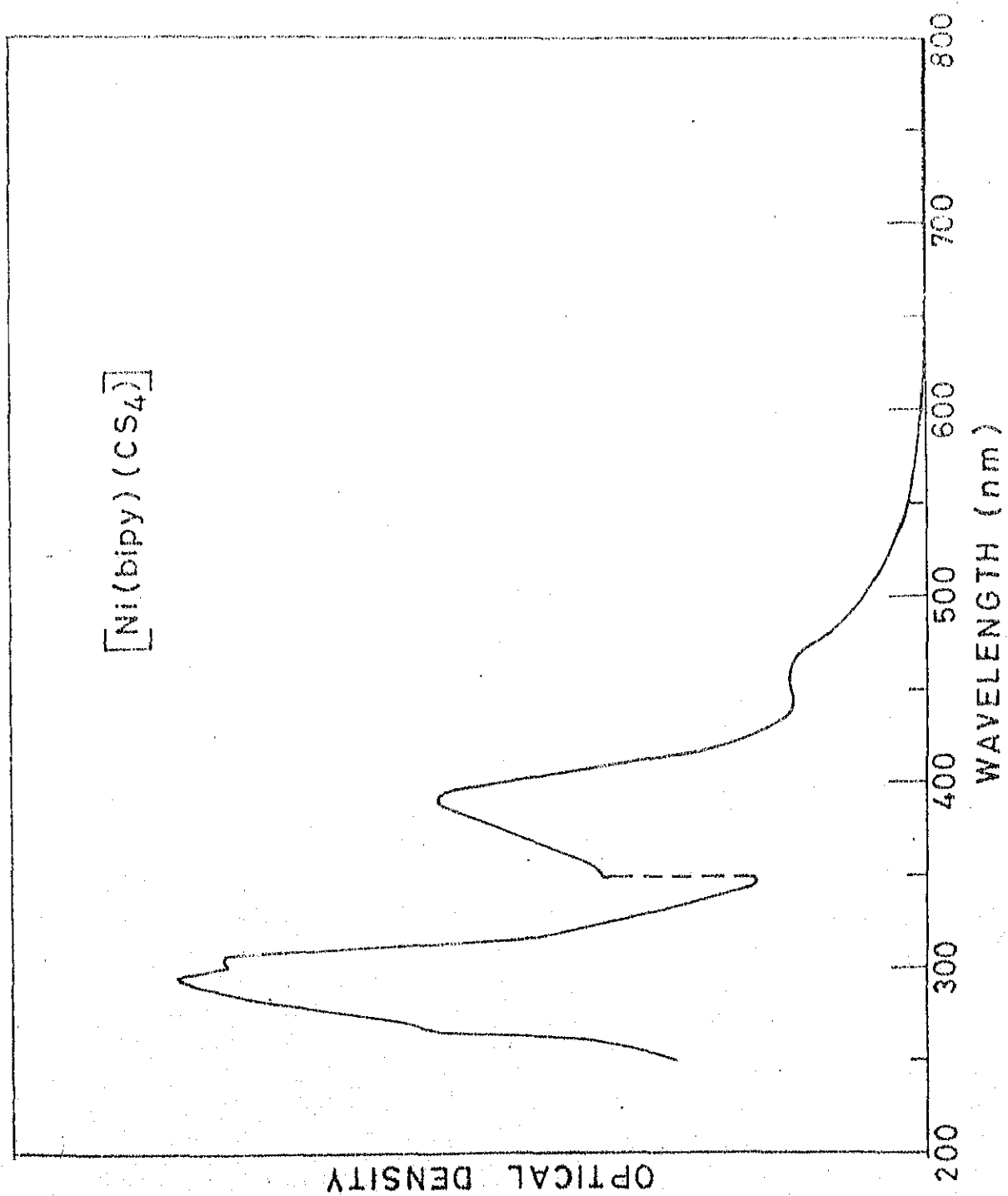
FIG.4.1.4





ELECTRONIC SPECTRUM

FIG. 4.1.5



ELECTRONIC SPECTRUM

FIG. 4.1.6

Table 4.1.1 Solid state electronic spectral data

Complex	$\lambda_{\text{max}}$ (nm)	Reference
$(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$	370, 480, 670	This work
$(\text{Et}_4\text{N})_2[\text{Ni}(\text{S}_4)_2]$	364, 469, 671	43
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$	405, 480, 585	This work
$(\text{Et}_4\text{N})_2[\text{PdS}_{11}]$	405, 515, 580	This work
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$	420, 520, 585	This work
$\text{Pd}(\text{o-phen})(\text{S}_4)$	390, 500	This work
$\text{Pd}(\text{bipy})(\text{S}_4)$	460(br)	This work
$\text{Ni}(\text{o-phen})(\text{S}_3\text{O}_2)$	395, 500, 535, 570	This work
$\text{Ni}(\text{bipy})(\text{S}_3\text{O}_2)$	415, 505, 540, 580	This work

Table 4.1.2 Electronic spectral data

Complex	Solvent	$\lambda_{\max}$ (nm)	( $\epsilon$ )	Reference
$(PPh_4)_2[Ni(CS_4)_2]$	$CH_2Cl_2$	318	$(1.87 \times 10^4)$	This work
		360sh	$(1.26 \times 10^4)$	
		388	$(1.57 \times 10^4)$	
		458	$(5.80 \times 10^3)$	
$(AsPh_4)_2[Ni(CS_4)_2]$	DMSO	314	$(1.60 \times 10^4)$	179
		359sh	$(1.30 \times 10^4)$	
		389	$(1.60 \times 10^4)$	
		463	$(5.20 \times 10^3)$	
$(PPh_4)_2[Ni(COS_3)_2]$	$CH_2Cl_2$	317	$(1.36 \times 10^4)$	This work
		375sh	$(1.19 \times 10^4)$	
		388	$(1.29 \times 10^4)$	
		455	$(4.00 \times 10^3)$	
$(AsPh_4)_2[Pd(CS_4)_2]$	$CH_2Cl_2$	300		This work
		325sh		
		360		
		437sh		
$(Et_4N)_2[Pd(COS_3)_2]$	$CH_2Cl_2$	330sh		This work
		360		
$Ni(o\text{-phen})(CS_4)$	DMF	312sh	$(9.55 \times 10^3)$	This work
		345sh	$(4.88 \times 10^3)$	
		370sh	$(5.28 \times 10^3)$	
		391	$(6.54 \times 10^3)$	
		458	$(1.59 \times 10^3)$	
$Ni(bipy)(CS_4)$	DMF	306	$(1.99 \times 10^4)$	This work
		325sh	$(9.36 \times 10^3)$	
		370sh	$(5.65 \times 10^3)$	
		391	$(6.83 \times 10^3)$	
		458	$(1.92 \times 10^3)$	

different synthetic route. Similarly the solution spectrum of  $[\text{Ni}(\text{CS}_4)_2]^{2-}$  agrees well with that reported by Coucouvanis and Fackler [179] prepared by a different synthetic procedure.

The characteristic features of the monoanionic complexes containing the chromophore  $\text{MS}_4$  are the intense absorption in the visible and near infrared regions. As described earlier these bands are not of d-d type but have their origin in some form of charge transfer. The assignment of the spectral features of square-planar dithiolene complexes has been carried out using an extended and simplified molecular orbital scheme by Gray and coworkers [196,197] and is presented in Fig. 4.1.7. The support for this scheme and electronic configuration was drawn mainly from the electronic spectra of the di- and monoanionic dicyano-dithiolene complexes. It is estimated that the  $4a_g$  and  $3b_{1g}$  levels are 26.0 and 55.7 per cent metal in character, respectively. Thus, for the monoanionic complexes the  $4a_g$  level could be singly occupied. It is stated that the  $4b_{2g}$  and  $4a_g$  levels are definitely more ligand than metal in character while the  $3b_{2g}$  and  $2a_g$  levels which are bonding are localized on the metal. The  $3b_{3g}$ ,  $3a_g$  and  $3b_{2g}$  orbitals are also largely metal in character. For a free  $d^8$  shell in all dithiolene complexes the orbitals labelled d in Fig. 4.1.7 are regarded as filled with metal electrons. It is observed that in the complexes containing incompletely filled  $4a_g$  and  $4b_{2g}$  levels the oxidation state of the metal

<u><math>3a_u, 4b_{3g}</math></u>	$L(\pi^*)$	$L(\pi^*)$
<u><math>3b_{1g}</math></u>	$XY$	$\sigma^*$
<u><math>4a_g</math></u>	$x^2-y^2$	$\pi_1^*$
<u><math>4b_{2g}</math></u>	$XZ$	$\pi_2^*$
<u><math>3b_{1g}, 2b_{2u}, 2b_{3u}, 2b_{1g}</math></u>	$L(\pi)$	$L(\pi)$
<u><math>3b_{3g}</math></u>	$YZ$	$d$
<u><math>3a_g</math></u>	$z^2$	$d$
<u><math>3b_{2g}</math></u>	$XZ$	$d$
<u><math>2a_g</math></u>	$x^2-y^2$	$d$
<u><math>1b_{2u}, 1b_{3u}, \text{etc.}</math></u>	$L(\sigma^-)$	$L(\sigma^-)$

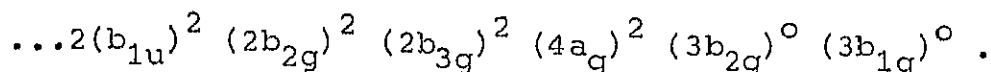
THE MO SCHEME FOR  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-1,-2}$

FIG. 4.1.7

can not be described correctly by classical oxidation state formalism. Thus, for monoanionic complexes the ground state configuration would be

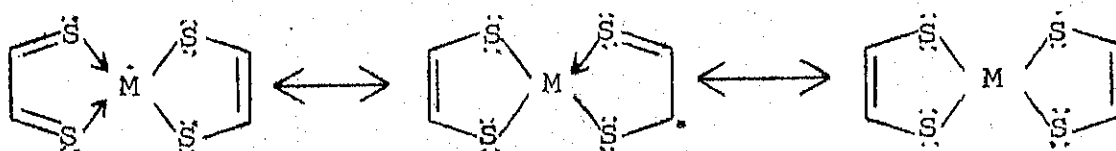
$$\dots(4b_{2g})^2 (4a_g)^1 .$$

It is suggested that this type of complex can also be represented as a derivative of  $M(II)(d^8)$  containing one dianionic dithiolato ligand and one spin free radical monoanionic ligand. An alternative description of the ligands in this situation is to regard them, as a whole, a partially oxidized trianion,  $(S_4C_4R_4)^{3-}$ . Contribution of metal character in the highest occupied molecular orbital can be made by using the hyperfine splitting observed in the esr spectra of these complexes as described later (vide infra). Further information about the electronic structures of bis(1,2-dithiolene) complexes can be achieved by analyzing the essential features of the electronic structure of the neutral molecules like  $(MS_4C_4R_4)$ . It is believed that the lowest unoccupied ligand  $\pi$ -molecular orbitals interact with the central metal ion orbitals in these systems. The  $B_{1u}$  combination of these two ligand orbitals ( $D_{2h}$  symmetry) becomes stabilized on interaction with the metal  $np_z$  orbital whereas  $B_{2g}$  combination becomes weakly antibonding on interaction with the metal  $nd_{xz}$  orbital. The calculated ground state for such system is thus,



In the present situation the three upper most orbitals shown here consist of both metal and ligand characters and the  $4a_g$  level is now predominantly metal ( $nd_{x^2-y^2}$  symmetry),  $3b_{2g}$  ligand ( $nd_{xz}$  symmetry) and the  $3b_{1g}$  metal ( $nd_{xy}$  symmetry) in character, respectively.

On reduction of  $MS_4C_4R_4$ , the  $3b_{2g}$  orbital becomes half-filled in the monoanion and totally filled in the dianion. The complete filling of this level has the effect of conferring true dithiolate character on the sulfur ligands, so that the dianionic complexes are correctly represented as containing divalent metal ions complexed by two dianionic dithiolate ligands. In neutral and monoanionic species one can regard the presence of divalent metal ions complexed by oxidized dithiolate ligands (ligands having considerable dithioketonic character). The monoanions, thus, can be regarded in valence bond resonance forms as shown below:

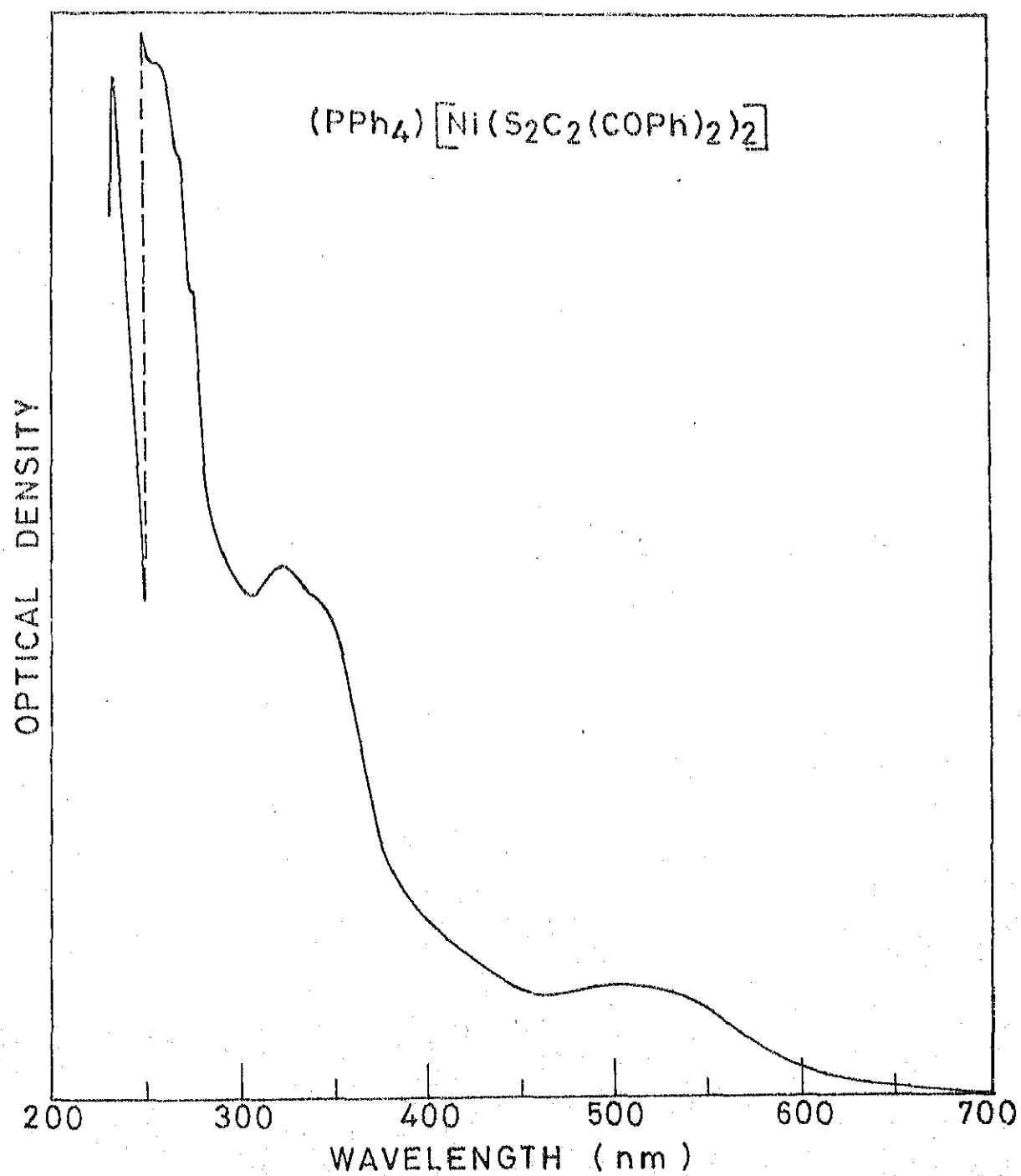


Thus, the C=C and S-C ( $sp_2$ ) bond lengths decrease and increase, respectively, as charge is added to the basic  $MS_4$  coordinated unit. As filling of the  $3b_{2g}$  level by electrons results in the conversion of the ligands from partially



dithioketonic form to a totally dithiolate form, structural changes should take place. Thus, the infrared stretching frequencies for the perturbed C=C and C=S stretching should increase and decrease, respectively (vide infra).

The electronic spectra of the monoanionic species and of  $[\text{Pd}(\text{o-phen})(\text{S}_2\text{C}_2(\text{COPh})_2)]$  are reproduced in Figs. 4.1.8 - 4.1.12 and the band positions are listed in Table 4.1.3. For comparison similar data from other dithiolene complexes are also presented in Table 4.1.3. It is interesting to note that the electronic spectra of the neutral and monoanionic complexes give very intense absorptions at low energy in the visible region. These strong absorptions are entirely absent in the spectra of the dianions indicating that their electronic structure is distinctly different from those of the more oxidized species. The major absorption at low energy in the monoanionic species is assigned to the transition  $2b_{1u} \rightarrow 3b_{2g}$ . This transition moves to lower frequencies compared to neutral species. This is because the  $2b_{1u}$  orbital like the  $3b_{2g}$  derives most of its character from ligand  $\pi$ -molecular orbitals and its absolute energy is dependent on a substituent effect. The dramatic effect of this can be seen when the substituent group changes from -COPh to -COOCH<sub>3</sub>. The remaining bands are described as of  $n_{\text{S}} \rightarrow \text{M}$ ,  $n_{\text{S}} \rightarrow \pi$ ,  $\text{M} \rightarrow \pi$  or  $\pi \rightarrow \pi$  type, the symbol  $n_{\text{S}}$  refers to transitions involving free electron pairs on the sulfur atom which are in the plane of the molecule



*ELECTRONIC SPECTRUM*

FIG. 4.1.8

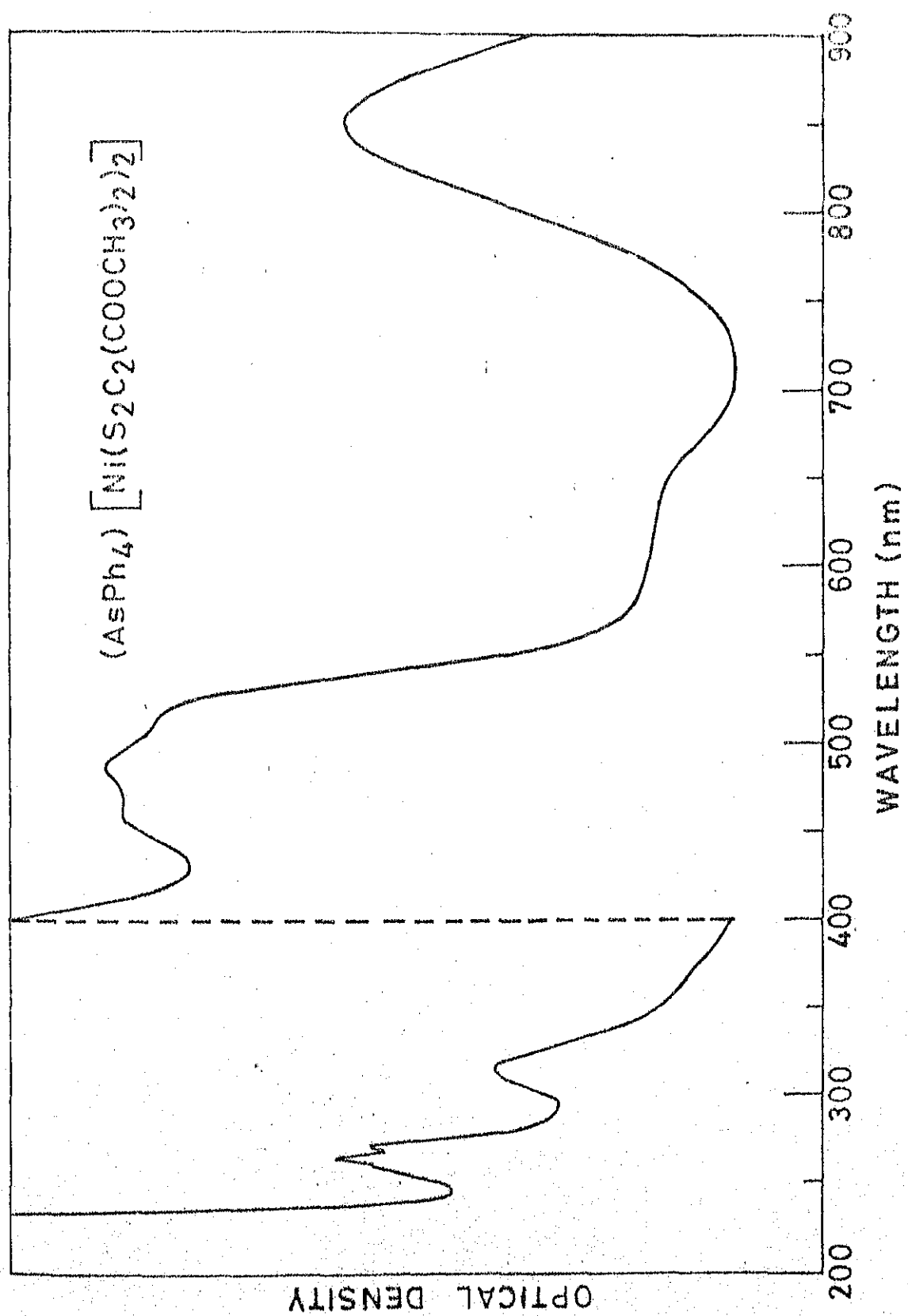
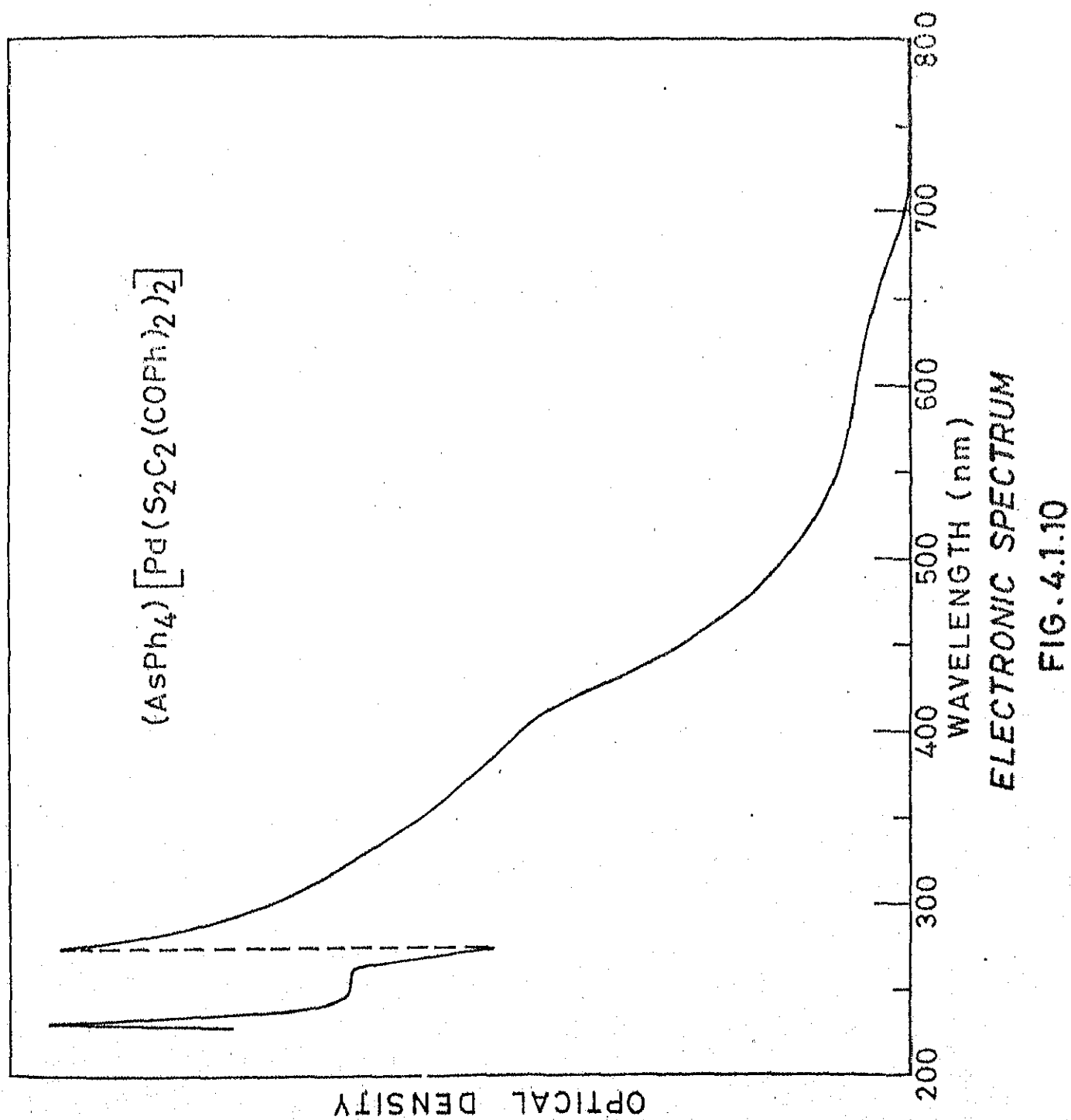
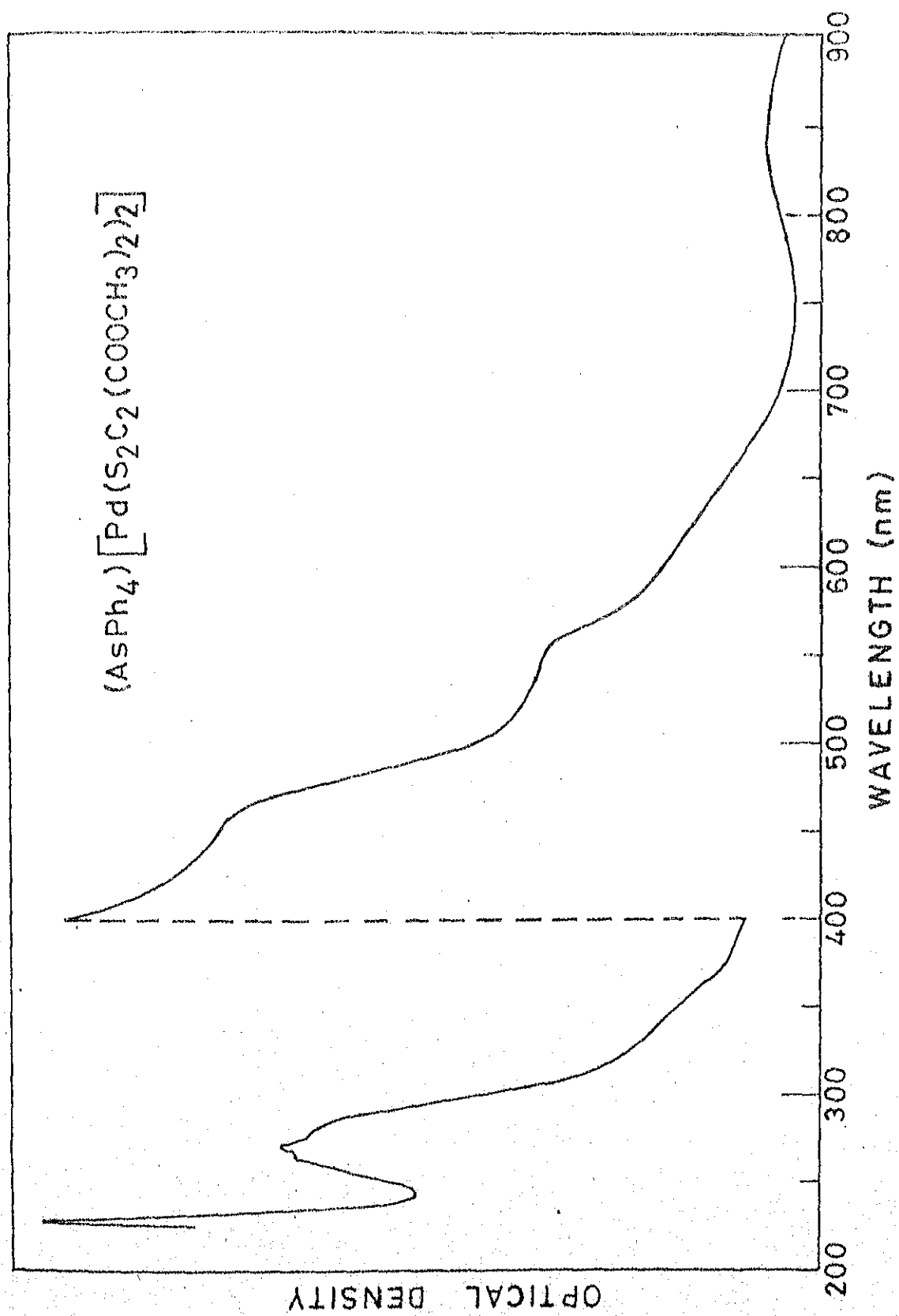


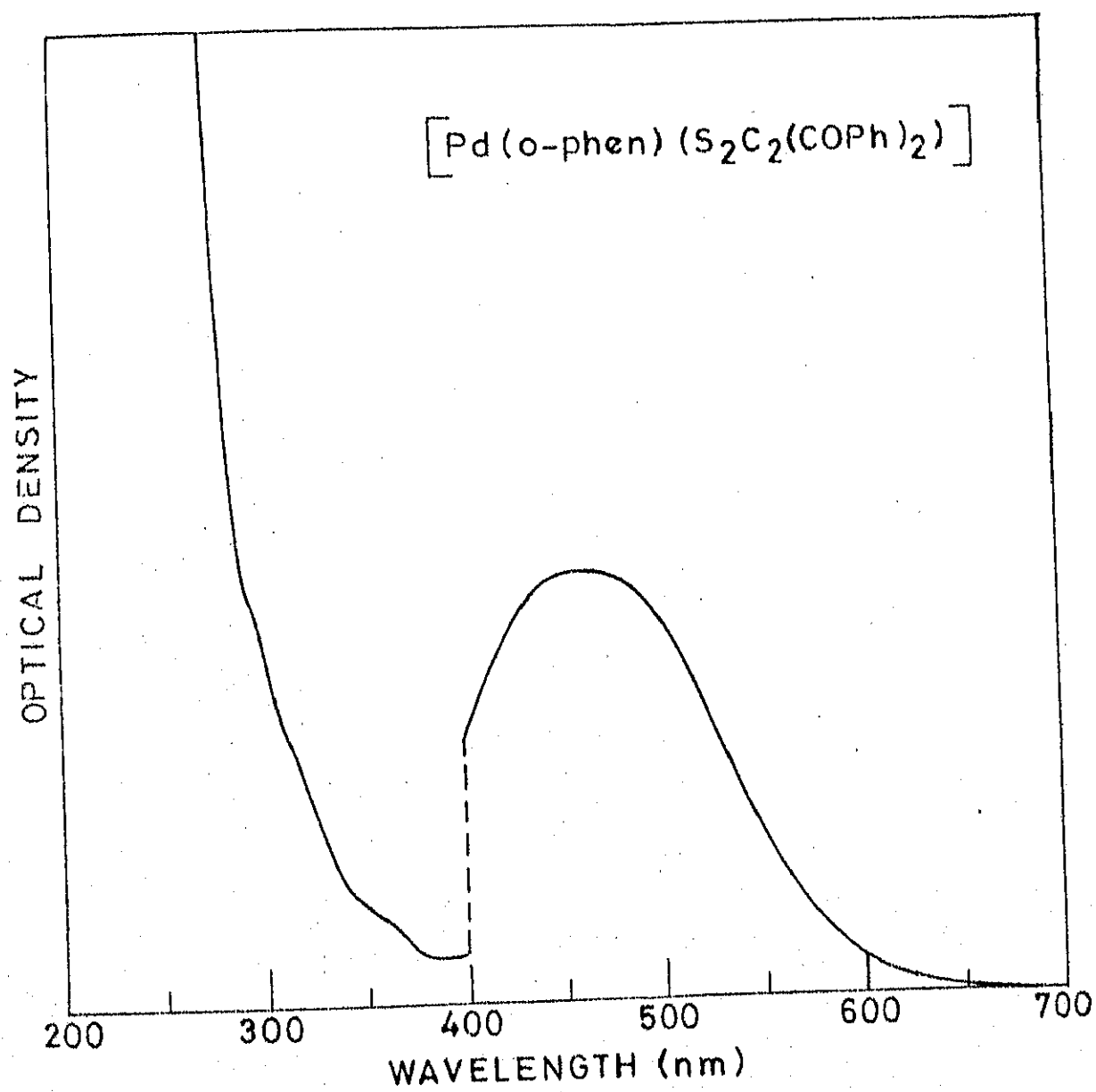
FIG. 4.1.9





ELECTRONIC SPECTRUM

FIG. 4.1.11



ELECTRONIC SPECTRUM

FIG. 4.1.12

Table 4.1.3 Electronic spectral data

Complex	Solvent	$\lambda_{\max}$ (nm)	( $\epsilon$ )	Reference
1	2	3	4	
$[\text{Ni}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^-$	$\text{CH}_2\text{Cl}_2$	322	$(1.44 \times 10^3)$	This work
		350sh	$(1.29 \times 10^3)$	
		410sh	$(4.50 \times 10^2)$	
		510	$(3.11 \times 10^2)$	
$[\text{Ni}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^-$	$\text{CH}_2\text{Cl}_2$	315	$(1.21 \times 10^4)$	This work
		370sh	$(4.96 \times 10^3)$	
		460	$(2.58 \times 10^3)$	
		485	$(2.63 \times 10^3)$	
		515sh	$(2.43 \times 10^3)$	
		645	$(5.75 \times 10^2)$	
$[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^-$	$\text{CH}_2\text{Cl}_2$	355sh	$(3.59 \times 10^4)$	This work
		405	$(1.25 \times 10^4)$	
		600	$(1.76 \times 10^3)$	
$[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^-$	$\text{CH}_2\text{Cl}_2$	350sh	$(1.05 \times 10^4)$	This work
		458	$(4.13 \times 10^3)$	
		555	$(1.95 \times 10^3)$	
		695sh	$(1.09 \times 10^3)$	
		845	$(3.75 \times 10^2)$	
$\text{Pd}(\text{o-phen})(\text{S}_2\text{C}_2)(\text{COPh})_2]$	DMF	312sh	$(7.02 \times 10^3)$	This work
		330sh	$(4.46 \times 10^3)$	
		362	$(2.23 \times 10^3)$	
		460br	$(2.23 \times 10^2)$	

Table 4.1.3 (contd.)

1	2	3	4
$[\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)]^-$	Pyridine	295	$(7.52 \times 10^3)$
		350	$(2.72 \times 10^3)$
		425sh	$(5.12 \times 10^2)$
		435	$(3.60 \times 10^2)$
		493sh	$(7.87 \times 10^2)$
		508	$(9.56 \times 10^2)$
		523sh	$(8.33 \times 10^2)$
		635	$(8.50 \times 10^1)$
		870	$(2.37 \times 10^3)$
		1150sh	$(3.23 \times 10^2)$
		1380sh	$(5.37 \times 10^1)$
$[\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)]^-$	THF	318	$(3.84 \times 10^4)$
		357sh	$(1.30 \times 10^4)$
		481	$(1.90 \times 10^3)$
		515sh	$(1.570 \times 10^3)$
		581	$(7.20 \times 10^2)$
		641	$(4.00 \times 10^2)$
		901	$(7.95 \times 10^3)$
$[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$	$\text{CH}_3\text{CN}$	314	$(4.24 \times 10^4)$
		366	$(1.37 \times 10^4)$
		481	$(2.50 \times 10^3)$
		545	$(6.90 \times 10^2)$
		599	$(5.00 \times 10^2)$
		848	$(8.00 \times 10^3)$
		1200	$(3.29 \times 10^2)$



but are at  $120^\circ$  to the M-S-C bond angles.

The Pd(IV) and Pt(IV) complexes are all low spin having the electronic configuration  $t_{2g}^6$ . For octahedral field the low spin ground state is  $^1A_{1g}$ . Two principal spin allowed absorption bands are to be expected corresponding to transition from the  $^1A_{1g}$  to the  $^1T_{1g}$  and  $^1T_{2g}$  excited states. Relative to 3d series these ligand field bands move to higher energies. No analogous electronic spectra of tris-substituted 1,2-dithiolene complexes containing formally  $4d^6$  or  $5d^6$  electronic configuration is reported. Considering the corresponding  $3d^6$  configuration, diamagnetic,  $[\text{Co}(\text{S}_6\text{C}_6(\text{CN})_6)]^{3-}$  anion has been studied [200,201]. A comparison of the reported spectrum of the above mentioned complex with analogous Co(III) compounds containing tris-bidentate ligands (conventional) reveals that there are few similarities between the two groups. Jørgensen has correlated the appearance of the first spin allowed band in the low-spin square-planar nickel(II) complexes at about the same energy as the first spin allowed band in the corresponding Co(III) complexes [202]. In some of the sulfur donor bidentate ligands this correlation has worked well, however, in the dicyanodithiolene systems it did not work as the first spin allowed band in  $[\text{Ni}(\text{S}_4\text{C}_4(\text{CN})_4)]^{2-}$  occurred at 848 nm and that in  $[\text{Co}(\text{S}_6\text{C}_6(\text{CN})_6)]^{3-}$  at 670 nm. According to the assignments of Schruzer and Mayweg [200], five types of transition would be expected in the electronic spectra of these

tris-dithiolenes, assuming  $D_{3h}$  symmetry. These are  $\pi \rightarrow \pi$ ,  $M \rightarrow \pi$ ,  $n_{\text{S}} \rightarrow \pi$ ,  $\pi \rightarrow M$  and d-d, but the first three of these would obscure the last two which are expected to be weak. Thus, it is very difficult to assign the transitions recorded for these species (Figs. 4.1.13 and 4.1.14). However, the molar absorption values of these bands suggest them as charge-transfer transition. It is expected that the transition responsible for  $M \rightarrow \pi$  should be metal dependent and would be expected to move to higher frequencies as the ionization potentials of the metal increases. Thus, characterization of this transition can be made on this argument and the data are tabulated in Table 4.1.4. It is important to note here that the actual geometry of these anions are not known which could range from trigonally distorted octahedra to trigonal-prismatic structure.

The electronic spectrum of  $[\text{Pd}(\text{S}_5)_3]^{2-}$  is reproduced in Fig. 4.1.15. The electronic spectral data of this complex anion along with that of  $[\text{Pt}(\text{S}_5)_3]^{2-}$  are tabulated in Table 4.1.4. For comparison the spectral data of free  $\text{S}_5^{2-}$  ion is also incorporated in Table 4.1.4. Once again the high molar absorption values of the bands observed in these tris-chelated complexes indicate them to be primarily of the charge transfer type. The influence of the metal ion to shift the charge transfer transitions of the free  $\text{S}_5^{2-}$  ion, when it is complexed, can be clearly seen. The only trend that can be seen here is

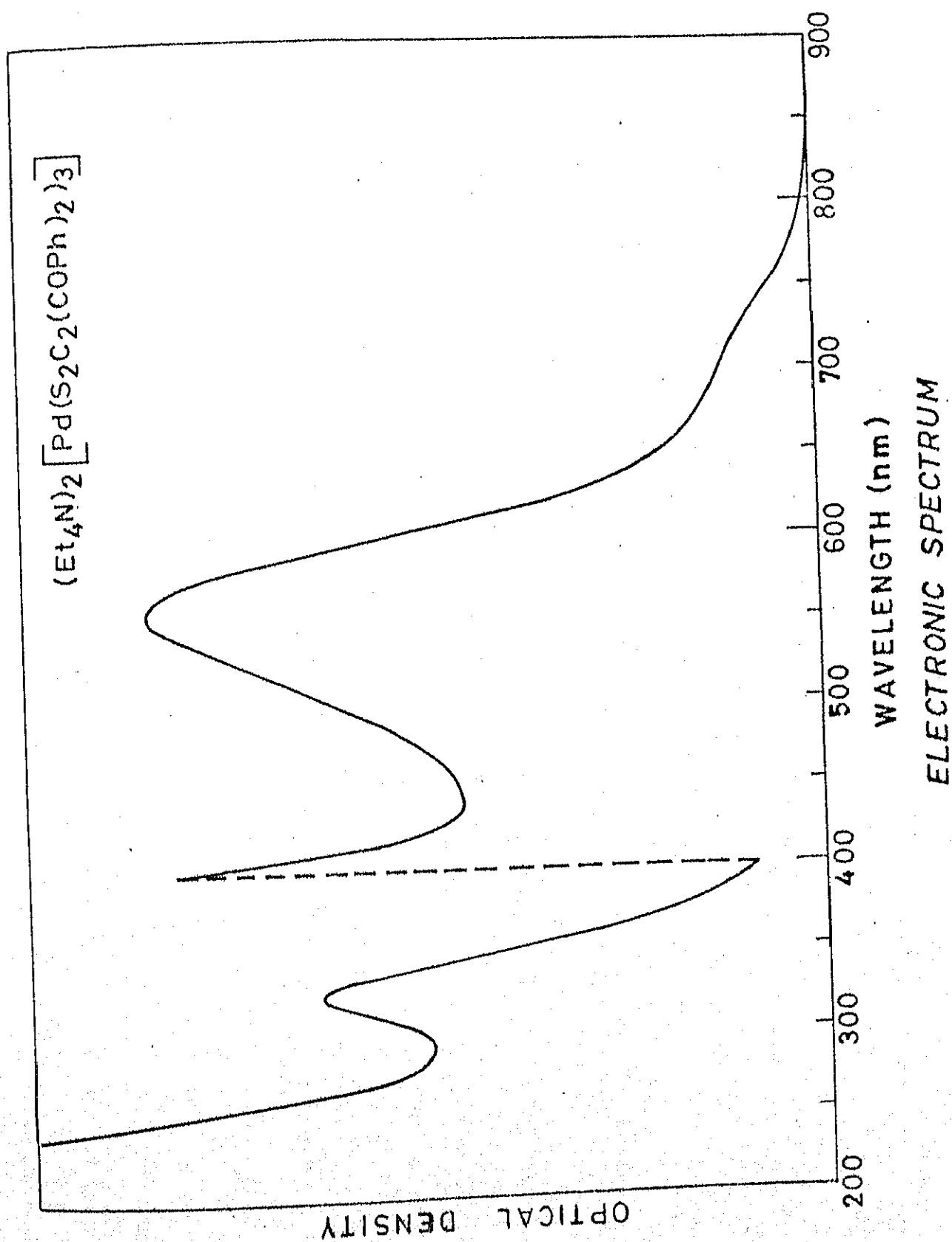
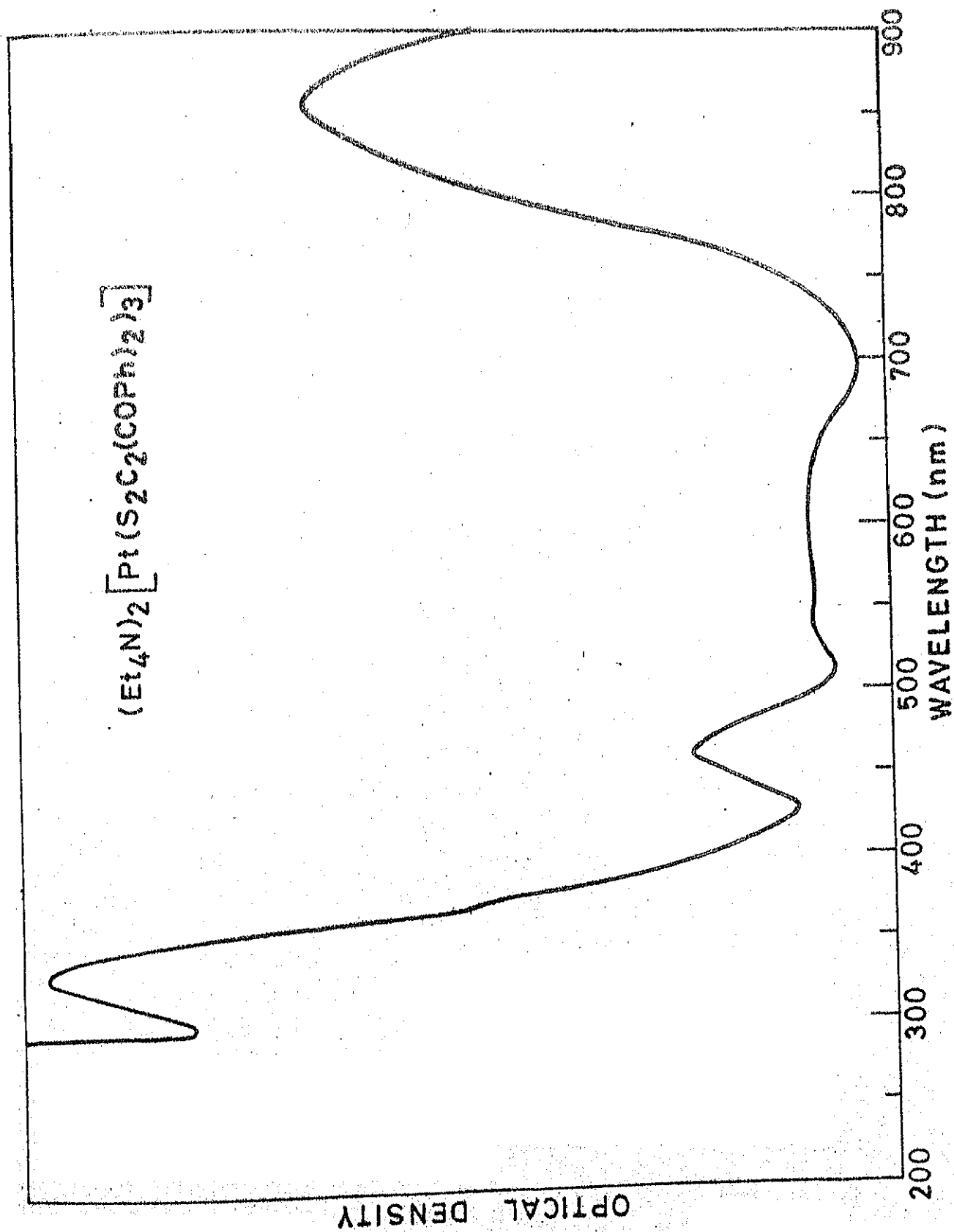
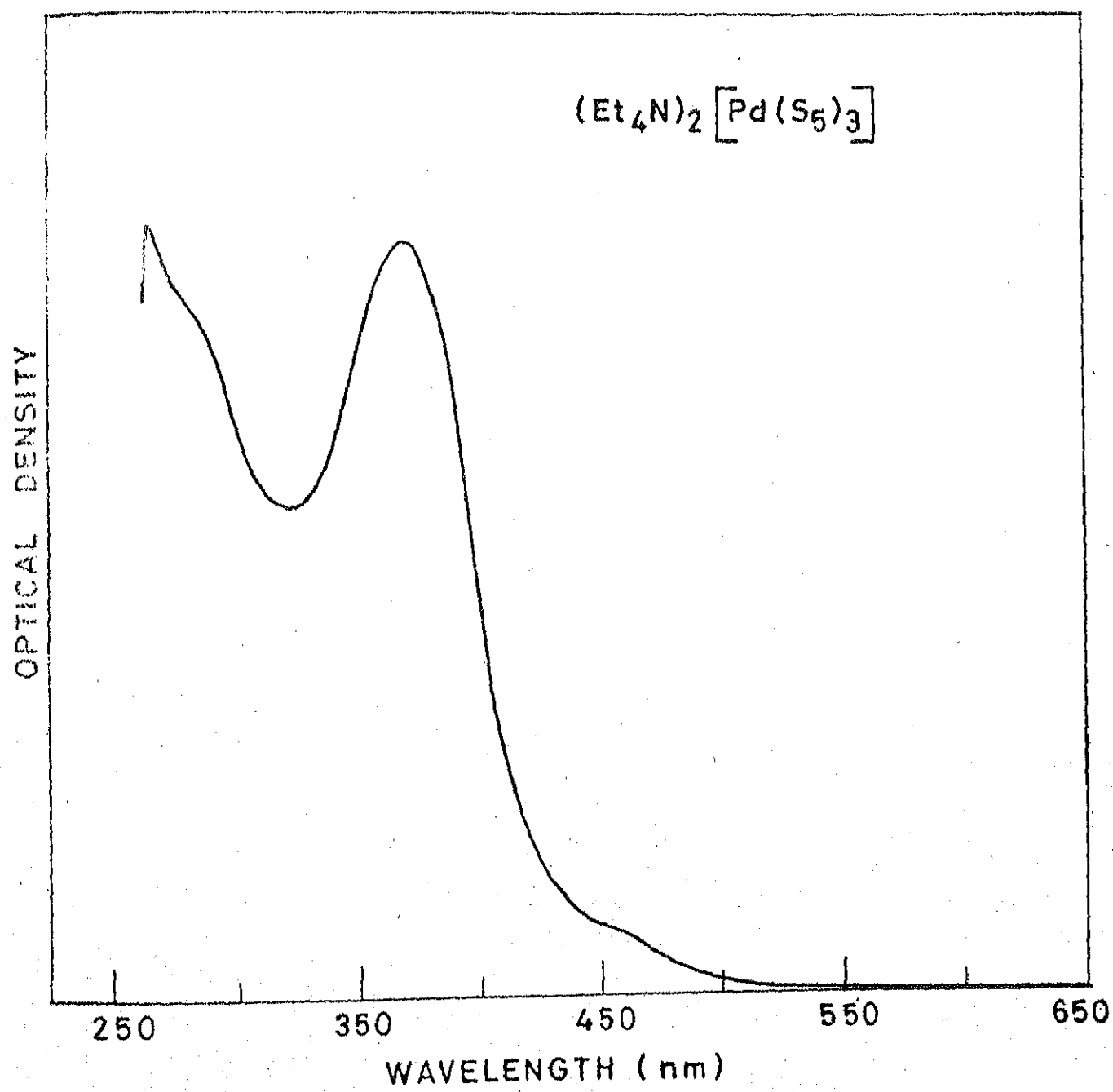


FIG. 4.1.13



ELECTRONIC SPECTRUM

FIG. 4.1.14



ELECTRONIC SPECTRUM

FIG. 4.1.15

Table 4.1.4 Electronic spectral data

Complex	Solvent	$\lambda_{\max}$ (nm)	( $\epsilon$ )	Ref.
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	DMF	325	$(4.61 \times 10^4)$	This work
		498sh	$(4.14 \times 10^3)$	
		557	$(6.10 \times 10^3)$	
		715sh	$(7.23 \times 10^2)$	
$(\text{AsPh}_4)_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$	$\text{CH}_2\text{Cl}_2$	339	$(8.76 \times 10^3)$	This work
		450	$(5.82 \times 10^3)$	
		530sh	$(1.80 \times 10^3)$	
		712	$(5.15 \times 10^2)$	
$(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	DMF	327	$(2.09 \times 10^4)$	This work
		350sh	$(1.87 \times 10^4)$	
		462	$(5.01 \times 10^3)$	
		543	$(1.84 \times 10^3)$	
		600br	$(1.93 \times 10^3)$	
		858	$(1.43 \times 10^4)$	
$(\text{AsPh}_4)_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$	$\text{CH}_2\text{Cl}_2$	300sh	$(1.93 \times 10^4)$	This work
		380sh	$(1.11 \times 10^4)$	
		$\sim 610\text{sh}$		
		$\sim 785\text{sh}$		
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$	DMF	368	$(2.77 \times 10^4)$	This work
		460sh	$(2.16 \times 10^3)$	
$(\text{NH}_4)_2[\text{Pt}(\text{S}_5)_3]$	$\text{H}_2\text{O}$	290	$(1.70 \times 10^4)$	56
		390	$(1.40 \times 10^4)$	
$(\text{NH}_4)_2\text{S}_5$	$\text{H}_2\text{O}$	250	$(3.00 \times 10^3)$	56
		375	$(1.00 \times 10^2)$	

the shift in the band positions of the palladium complex to lower energy side compared to that of the platinum compound.

#### 4.2 Vibration Spectra

The structural aspect of these polysulfido complexes can be reasonably determined using infrared and Raman spectroscopy. For the  $S_4^{2-}$  and  $S_5^{2-}$  complexes, the identification of S-S and M-S stretching vibrations apparently looks to be an easy job. However, in  $S_x^{2-}$  complexes except for  $S_2^{2-}$ , S-S mode of vibrations are generally weak in nature in the infrared. In addition, when these chelating ligands are bonded to metal centers having other coligands whose certain vibrations appear in this region, the task becomes more complicated. The S-S mode of vibrations of  $S_4^{2-}$  and  $S_5^{2-}$  appear in the region  $500\text{--}375\text{ cm}^{-1}$ . For the M-S stretching mode, medium to weak intensity bands appear around  $300\text{ cm}^{-1}$  depending upon the oxidation state of the metal ion, the other ligands present and the symmetry of the complex.

The infrared spectra of the synthesized complexes containing only tetrasulfide ligands are reproduced in Figs. 4.2.1 and 4.2.2. For  $(PPh_4)_2[Ni(S_4)_2]$ , a weak band at  $280\text{ cm}^{-1}$  has been assigned to  $\nu_{as}(\text{Ni-S})$  and the bands at 480, 430, and  $370\text{ cm}^{-1}$  could be due to the S-S modes of vibration of the  $S_4^{2-}$  ligand. This assignment is in good agreement with the data reported by Müller and coworkers [43]. For the

corresponding palladium complex  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$ , a band at  $280\text{ cm}^{-1}$  has been assigned to  $\nu_{\text{as}}(\text{Pd}-\text{S}_4)$ . A band at  $315\text{ cm}^{-1}$  has been assigned to the corresponding symmetric mode of vibration. It is apparently confusing to note that the asymmetric metal-sulfur stretching vibrations for the nickel(II) and its higher congener palladium(II) complexes are identical. A simple mass effect relationship should speak that Pd-S stretching should be slightly lower than the Ni-S stretching vibration. However, this type of argument is well understood when ligands used are of conventional type. Though, both the complexes are isomorphous in nature [43], the softness of palladium makes the palladium-sulfur bond stronger compared to that of nickel-sulfur bond. This effect apparently counters off the lowering of  $\nu(\text{Pd}-\text{S})$  over  $\nu(\text{Ni}-\text{S})$ . This view is further corroborated by studying the infrared spectra of the substituted species like  $[\text{M}(\text{L-L})(\text{S}_4)]$  (where  $\text{M} = \text{Ni}$  or  $\text{Pd}$  and  $(\text{L-L}) = \text{o-phen}$  or  $\text{bipy}$ ). Thus, for  $[\text{Ni}(\text{o-phen})(\text{S}_4)]$  a band at  $320\text{ cm}^{-1}$  has been assigned to  $\nu(\text{Ni}-\text{S})$ . The Ni-N stretch arising from coordinated aromatic diimines are also generally weak in nature [203]. Similarly, for the analogous bipyridyl complex of nickel this vibration appears at  $335$  and  $315\text{ cm}^{-1}$ . For the corresponding palladium complexes the Pd-S stretching vibrations appear at  $335\text{ cm}^{-1}$  for  $[\text{Pd}(\text{o-phen})(\text{S}_4)]$  and at  $330\text{ cm}^{-1}$  for  $[\text{Pd}(\text{bipy})(\text{S}_4)]$ . A trend of increased  $\nu(\text{M}-\text{S})$  is observed for these derivatives. This trend can be explained using more flow of  $\pi$ -electron density to the metal center which



could be readily dissipated by the  $\pi$ -accepting capability of the aromatic diimines. As a consequence of this extra-flow of  $\pi$ -electron density from sulfur ligand to the metal center, the metal-sulfur stretching vibration becomes stronger and for that an upward trend can be anticipated. The back-bonding ability of certain coligands can also facilitate  $\pi$ -electron flow from sulfur to the metal center and the isolation of another substituted pentasulfido complex anion  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$ , speaks for it. For this compound a band at  $283\text{ cm}^{-1}$  is assigned to  $\nu(\text{Ni-S})$ . The very weak vibrations appearing at  $393$  and  $385\text{ cm}^{-1}$  are tentatively assigned to  $(\text{S-S})$ . The spectra of these substituted polysulfido complexes are reproduced in Figs. 4.2.3 to 4.2.7 and the band positions are tabulated in Table 4.2.1. The salient features of the infrared spectrum of  $(\text{Et}_4\text{N})_2^- [\text{Pd}(\text{S}_5)_3]$  (Figure 4.2.8) along with that of the corresponding platinum complex (Fig. 4.2.9) are listed in Table 4.2.1. A comparison of the two spectra clearly suggests that the band at  $302\text{ cm}^{-1}$  can be assigned to  $\nu(\text{Pd-S})$ . For the platinum compound  $\nu(\text{Pt-S})$  are observed at  $295$  and  $285\text{ cm}^{-1}$ . The spectrum of  $(\text{NH}_4)_2[\text{Pt}(\text{S}_5)_3]$  has been reported in the literature [56], where the bands at  $294$  and  $286\text{ cm}^{-1}$  are assigned to  $\nu(\text{Pt-S})$ . A point of concern here is that the  $\nu(\text{Pd-S})$  vibration is not split unlike that of  $\nu(\text{Pt-S})$ . The structure of the platinum complex is known and the site symmetry is roughly octahedral. High symmetry could be accounted for less splitting ( $\sim 10\text{ cm}^{-1}$ ) in the platinum complex. However, to resolve the ambiguity

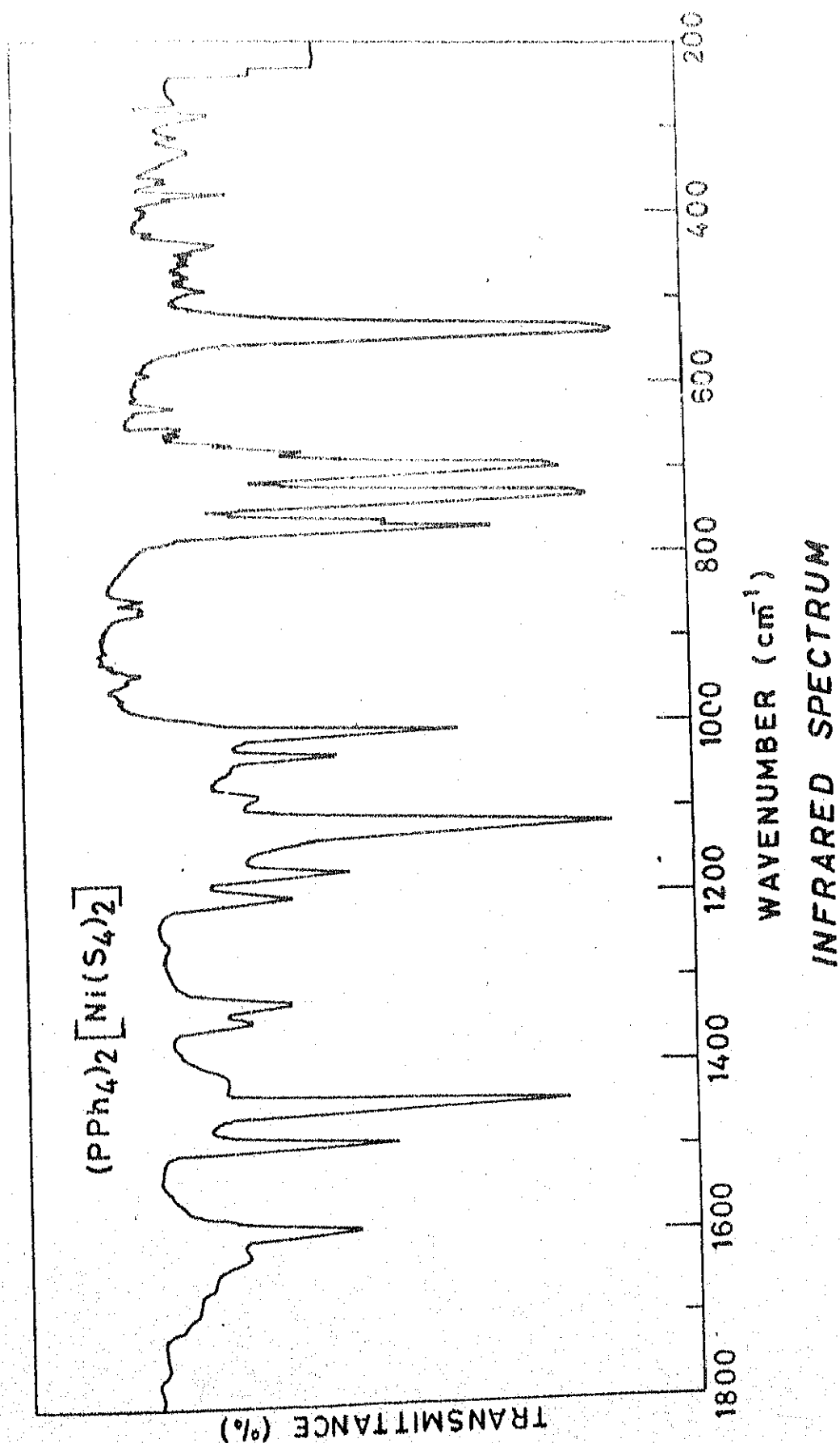
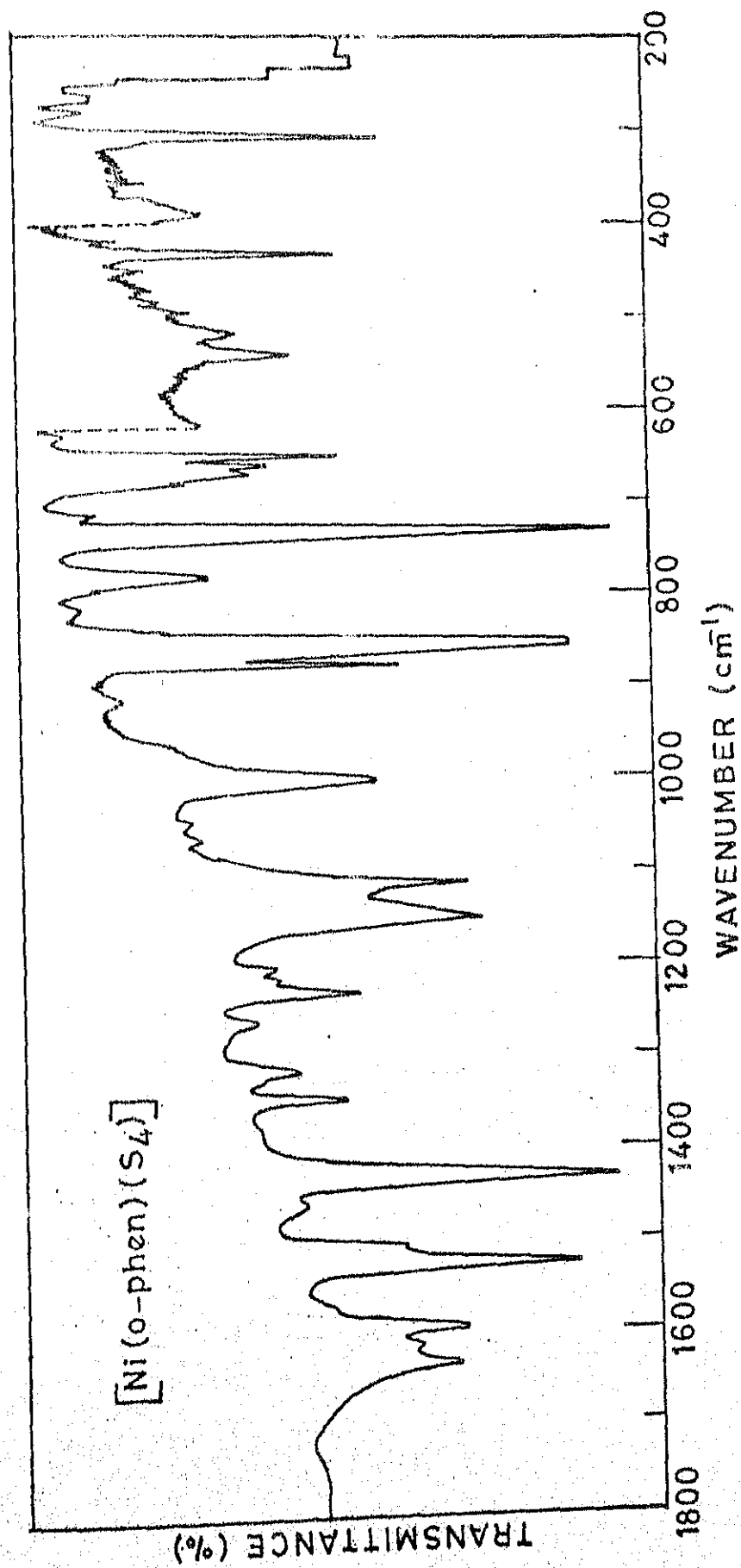
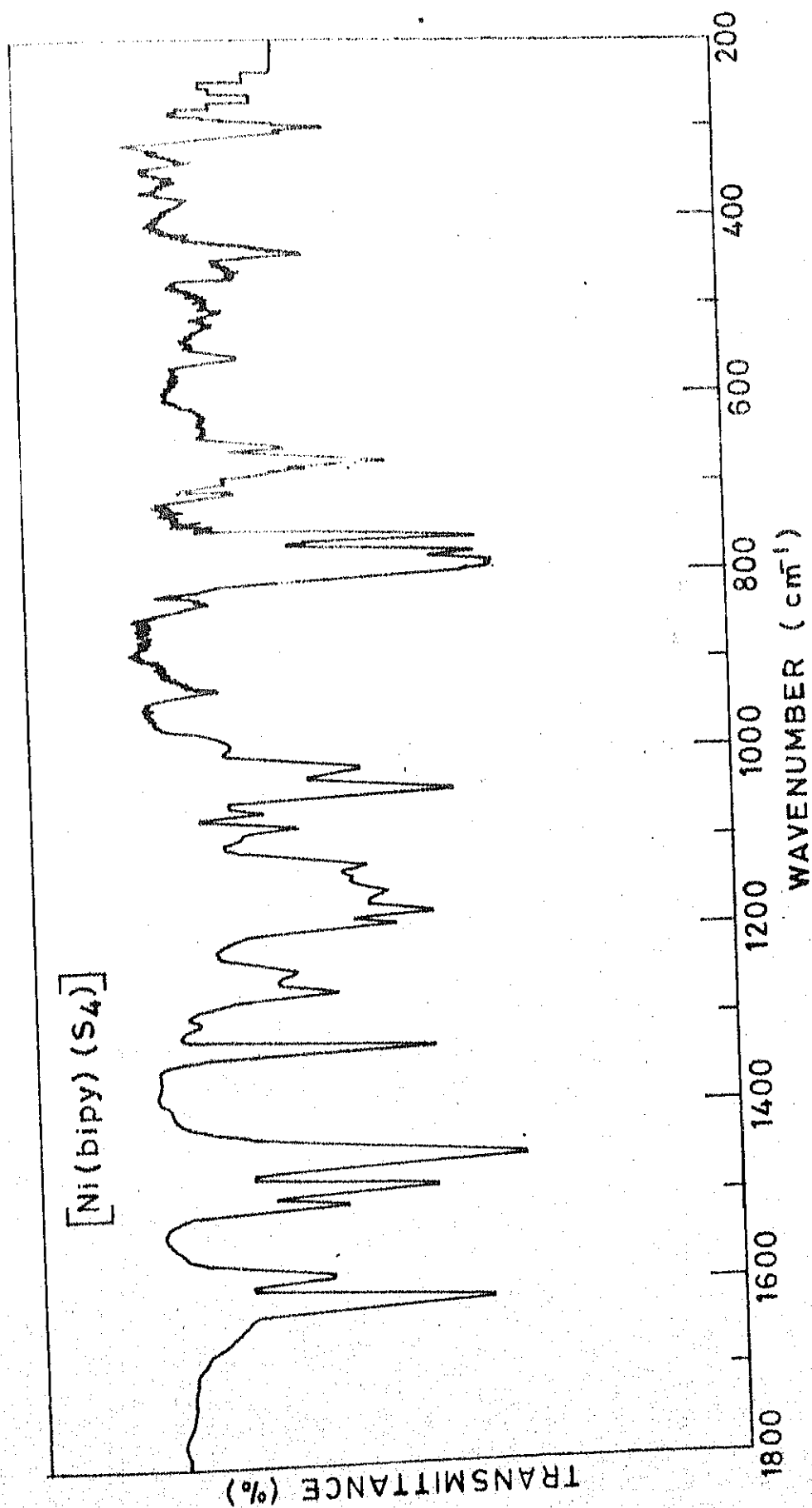


FIG. 4.2.1



INFRARED SPECTRUM

FIG. 4.2.3



INFRARED SPECTRUM

FIG. 4.2.4

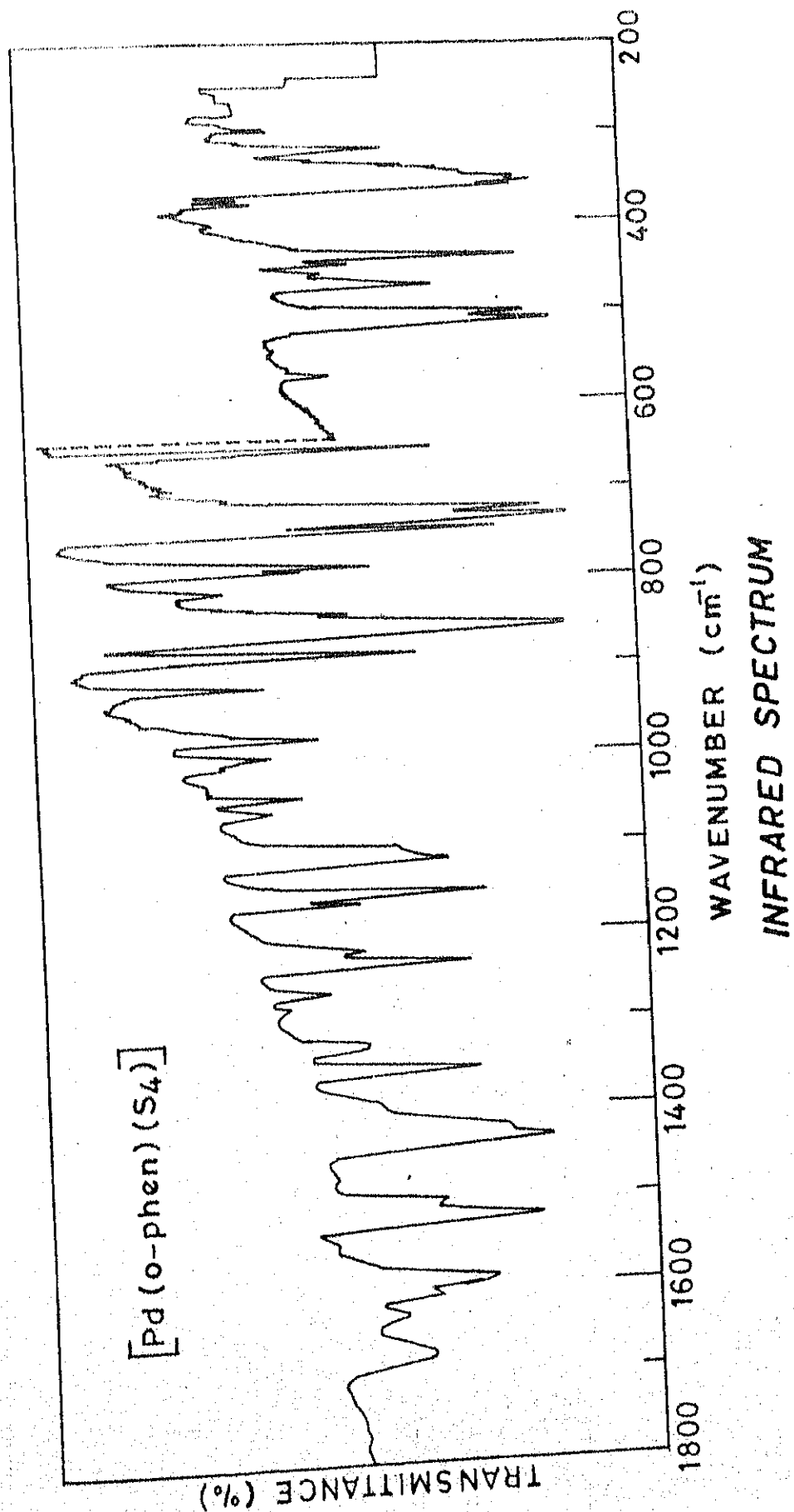
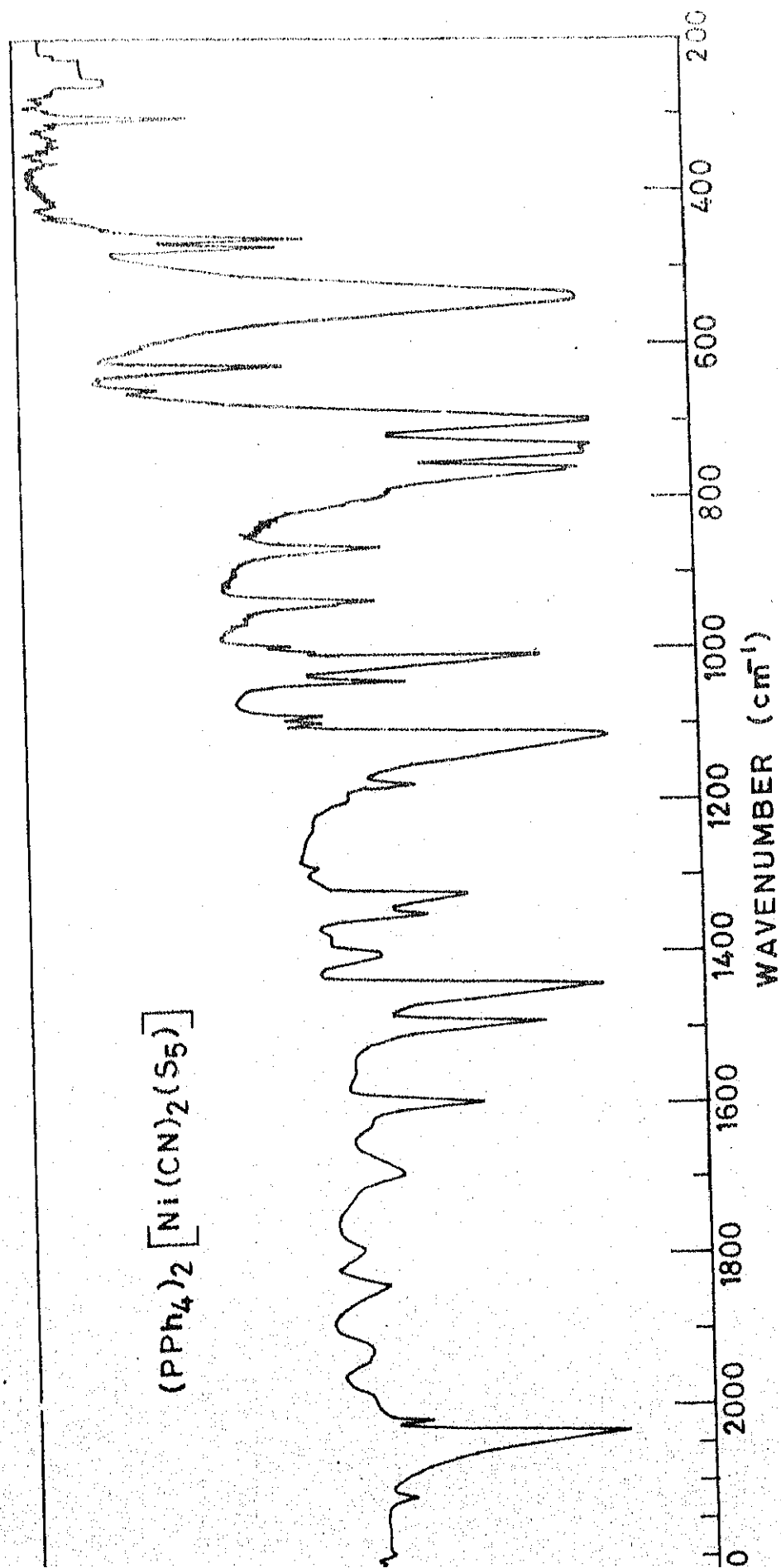
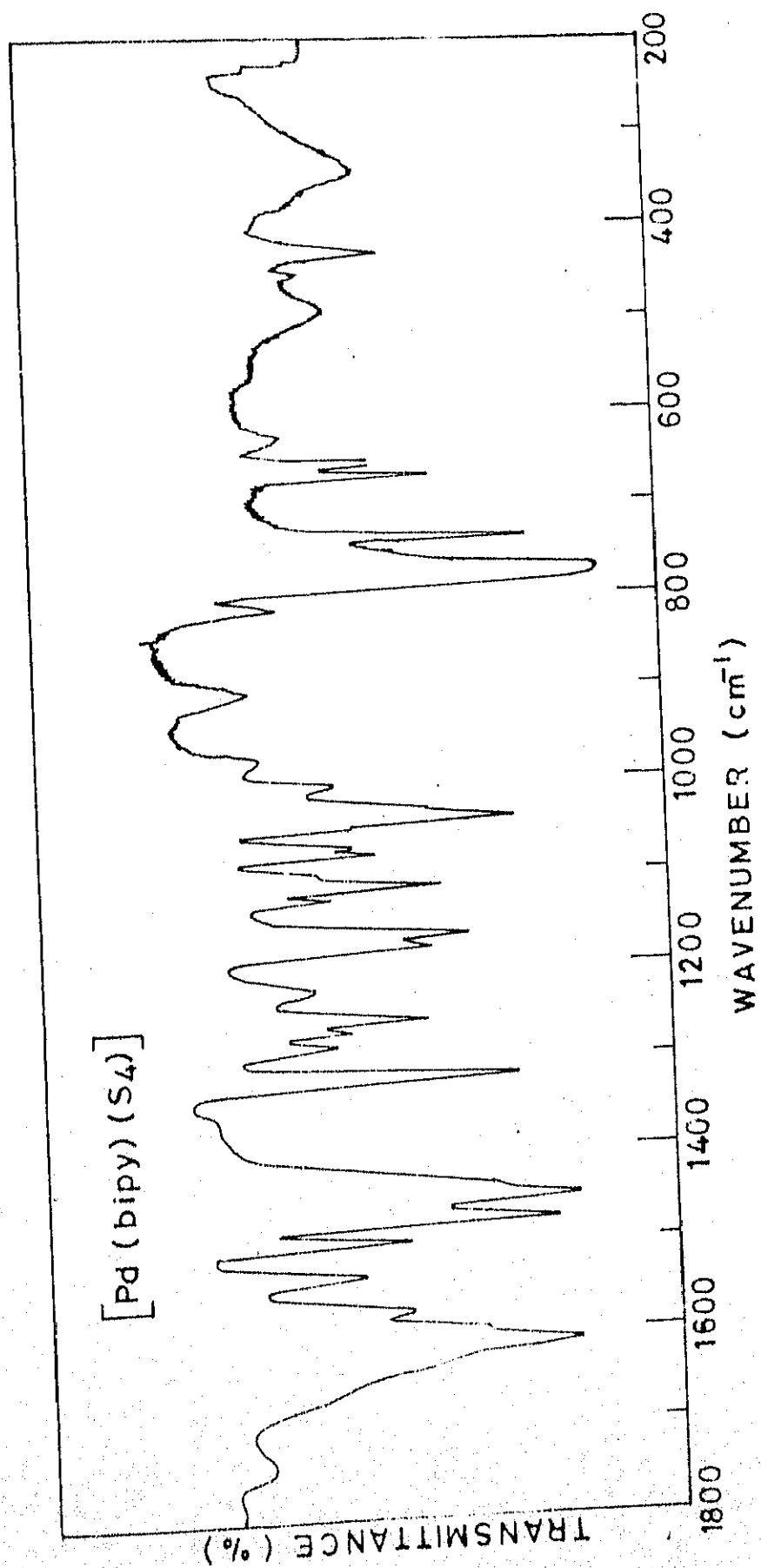


FIG. 4.2.5



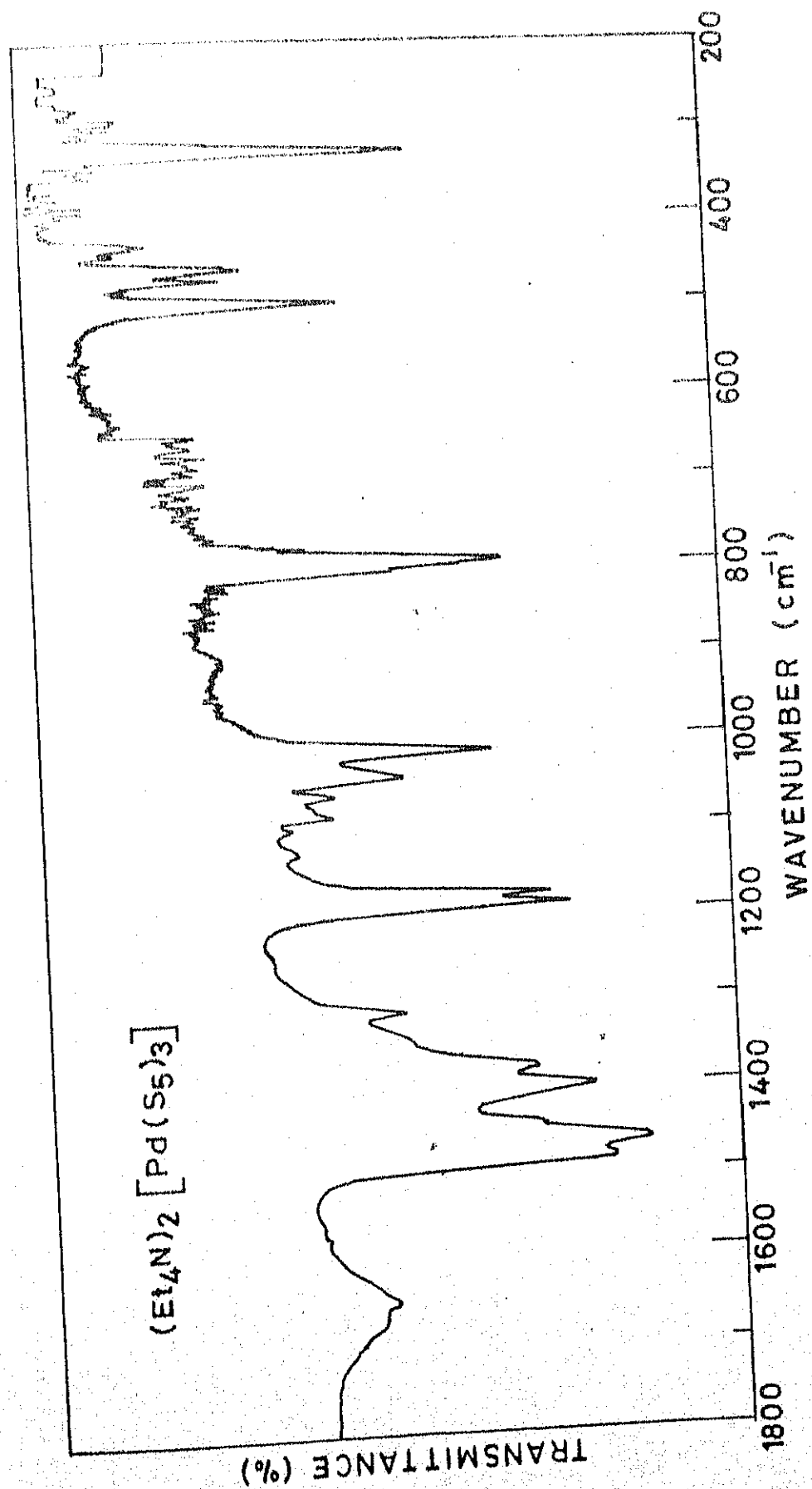
INFRARED SPECTRUM

FIG. 4.2.6



INFRARED SPECTRUM

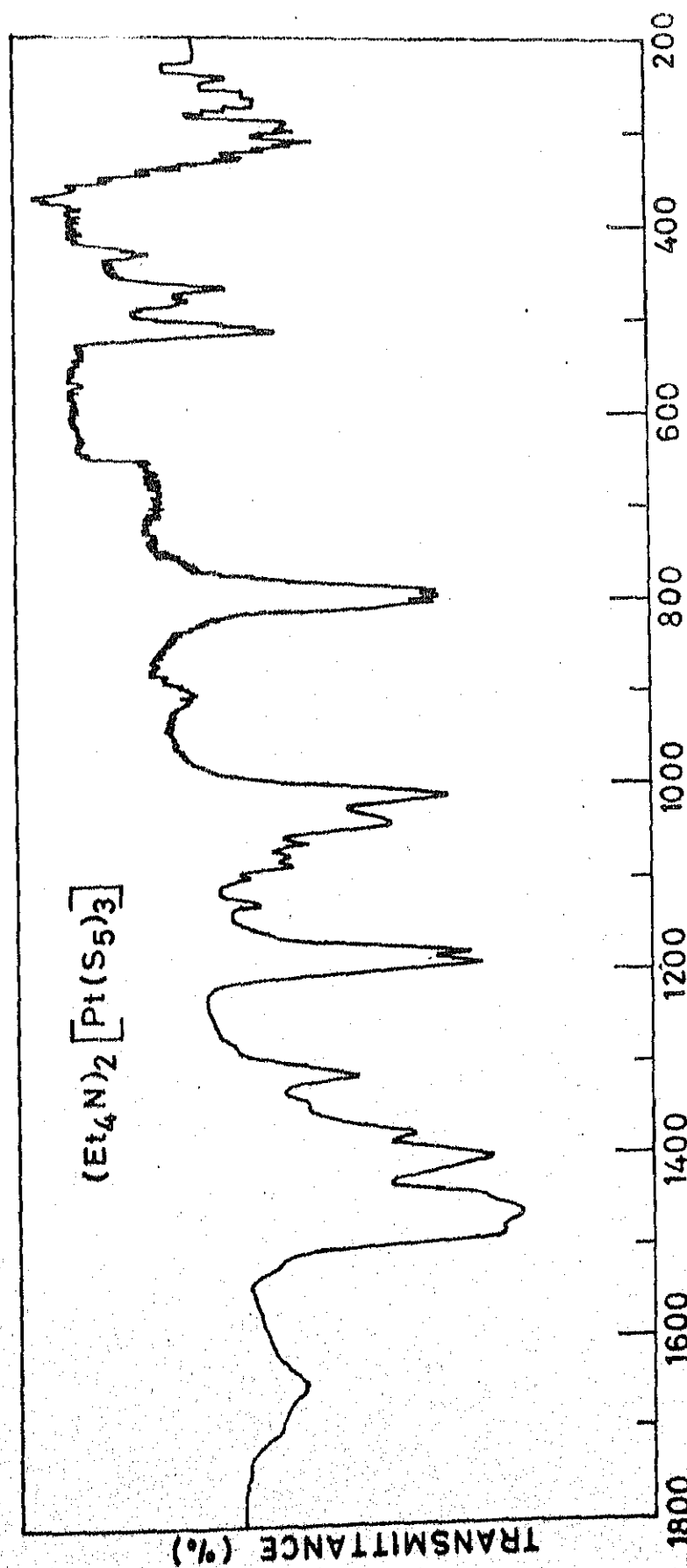
FIG. 4.2.7



INFRARED SPECTRUM

FIG. 4.2.8





INFRARED SPECTRUM

FIG. 4.2.9

Table 4.2.1 vibration spectral data of polysulfido complexes<sup>a</sup>

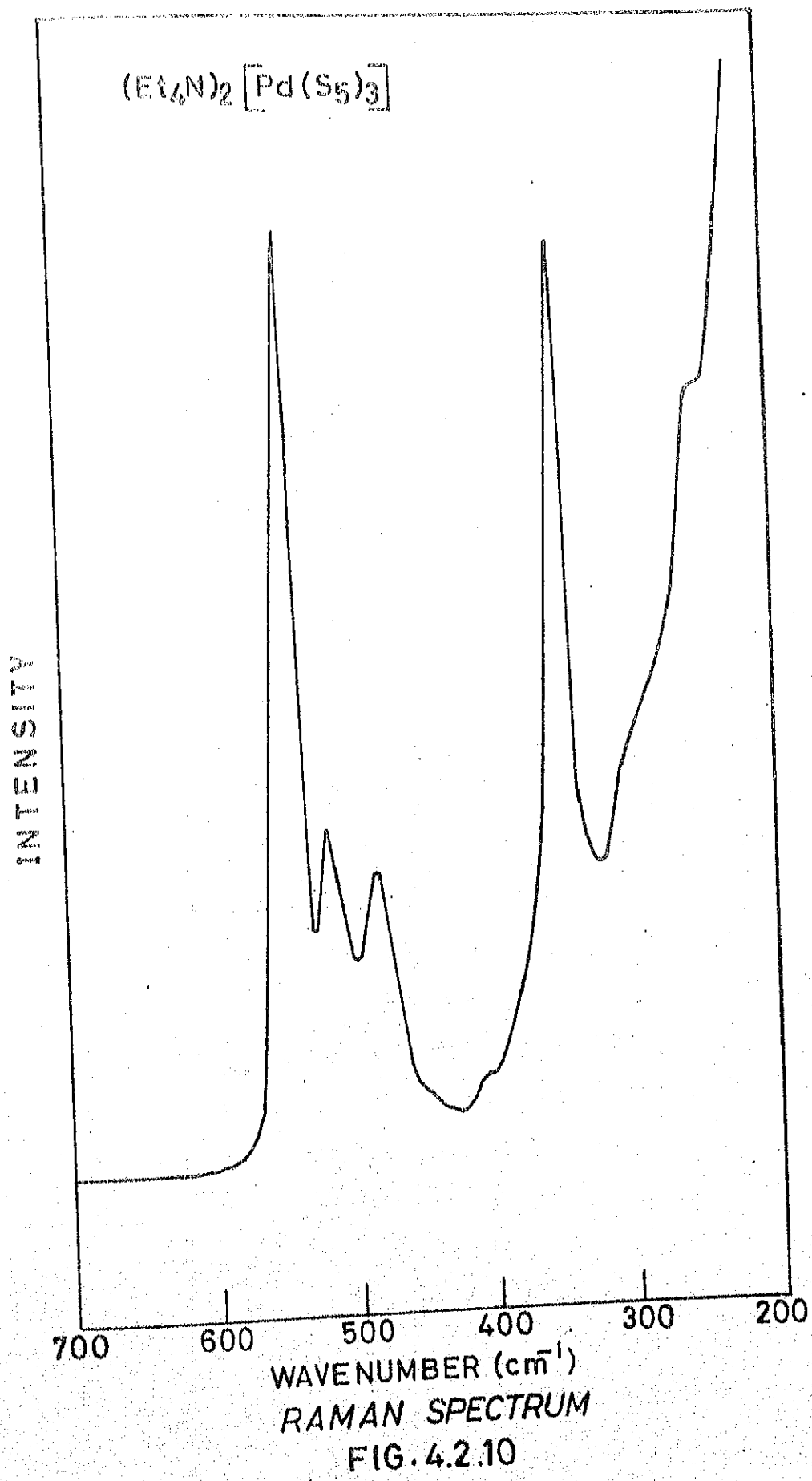
Complex	$\nu(\text{S-S})$ ( $\text{cm}^{-1}$ )	$\nu(\text{M-S})$ ( $\text{cm}^{-1}$ )	Other important frequencies ( $\text{cm}^{-1}$ )
$(\text{PPh}_4)_2[\text{Ni}(\text{S}_4)_2]$	480, 430, 370	280	-
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_4)_2]$	480, 449, 432, 405	314, 280	-
$(\text{Et}_4\text{N})_2[\text{PdS}_{11}]$	510, 480	300	-
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$	480, 451, 440, 410, 480 <sup>b</sup> , 543 <sup>b</sup>	302, 350 <sup>b</sup>	-
$(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$	490, 461, 450, 410	295, 285	-
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$	393, 485	283	2110, 2070 ( $\nu_{\text{CN}}$ ) 450, 440 ( $\nu_{\text{NiC}}$ )
$\text{Ni}(\text{o-phen})(\text{S}_4)$	520, 500, 412, 380	320	290 ( $\nu_{\text{NiN}}$ )
$\text{Ni}(\text{bipy})(\text{S}_4)$	535, 440, 420, 360	335, 315	286, 280 ( $\nu_{\text{NiN}}$ )
$\text{Pd}(\text{o-phen})(\text{S}_4)$	495, 480, 450	335	280 ( $\nu_{\text{PDN}}$ )
$\text{Pd}(\text{bipy})(\text{S}_4)$	475, 445, 420	330	-

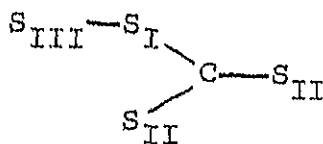
a, IR bands unless otherwise stated

b, Raman bands.

for the absence of split  $\nu(\text{Pd-S})$  we have recorded the Raman spectrum of  $(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_5)_3]$  (Fig. 4.2.10). The symmetric Pd-S stretching vibration appears at  $350\text{ cm}^{-1}$ . A careful checking of the infrared spectrum of this complex shows a weak band at  $340\text{ cm}^{-1}$  which could be due to symmetric  $\nu(\text{Pd-S})$ . The infrared spectrum of  $(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_5)_3]$  shows a broad contour of Pt-S stretching vibration which might be due to solid state effect. A difference in the spectra in this region suggests that the lattice containing these two might not be identical in nature. X-ray powder diffractograms of these two compounds suggest that they are not isostructural. The ambiguity could be resolved only when a three dimensional structural analysis of the palladium compound could be made. For the S-S mode of vibrations arising from the coordinated  $\text{S}_5^{2-}$  ligand, the i.r. spectral features are same for both the compounds. In the Raman spectrum a strong band at  $543\text{ cm}^{-1}$  and two weak bands at  $520$  and  $480\text{ cm}^{-1}$  appear besides  $\nu_{\text{as}}(\text{Pd-S})$ . The band at  $520\text{ cm}^{-1}$  may be due to cation and at  $480\text{ cm}^{-1}$  is due to  $\nu_{\text{as}}(\text{S-S})$ . The band at  $543\text{ cm}^{-1}$  is a symmetric vibration arising due to  $\nu(\text{S-S})$ . The band positions for the S-S vibrations are tabulated in Table 4.2.1.

The infrared spectra of complexes containing the coordinated perthiocarbonate ligand are reproduced in Figs. 4.2.11 - 4.2.14 and the important band positions are listed in Table 4.2.2. The perthiocarbonate ion has a nontetrahedral structure as shown below :





and the planarity of this ion has been established using Hückel MO method [204]. Hence the delocalization of the  $\pi$ -electron density could be anticipated when this ligand is chelated to a metal centre. The infrared spectrum of the ammonium salt of this ion shows four bands of medium intensity each at 955, 825, 510 and 485  $\text{cm}^{-1}$  [204]. The bands at 955 and 825  $\text{cm}^{-1}$  are assigned to  $A_1$  and  $B_1$  vibrations which arise from  $\nu_3(E')$  vibration of trithiocarbonate ion by reducing its symmetry ( $C_{2v}$ ). These are not pure stretching vibrations but a mixture of both  $\nu(C=S_I)$  and  $\nu(C=S_{II})$  vibrations. The bands at 519 and 485  $\text{cm}^{-1}$  are assigned to a symmetric vibration ( $A_1$ ) of the whole  $CS_I(S_{II})_2$  group and for a deformation vibration of  $B_2$  mode. It is difficult to pinpoint which vibrations arise from  $A_1$  mode and  $B_1$  mode. For the free ion it is difficult to notice any  $\nu(S-S)$ , which should normally appear in the region 500-400  $\text{cm}^{-1}$ , since they are very weak in nature. However, the formation of coordinated  $CS_4^{2-}$  by the interaction of polysulfido metal complexes with carbon disulfide can be thought of as an insertion reaction with the concomitant cleavage of S-S bond in the coordinated polysulfide group. When the  $CS_4^{2-}$  is bonded in a chelated fashion, the symmetry of the coordinated ion is lower than the free ion. Interestingly the coordination of

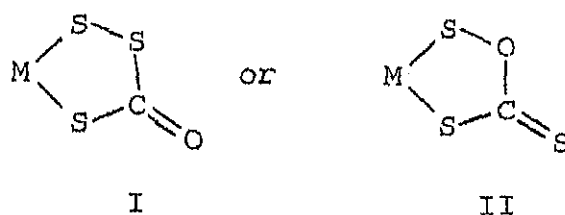
$\text{CS}_4^{2-}$  to a metal center via the perthio group [131] should cause the  $\nu(\text{S-S})$  infrared active because a large dipole moment change is expected for the S-S vibration in the closed cyclic structure. Thus, it is apparent that when  $\text{CS}_4^{2-}$  is coordinated as bidentate ligand the infrared spectrum is going to be more complicated and as most of the vibrations can mix with one other, no meaningful analysis can be made. However, for characterization purposes one can still identify the  $\nu(\text{C=S})$  vibration as one of the free  $\text{C=S}_{\text{II}}$  of the uncoordinated ion gets in the ring via sulfur coordination. Recently for coordinated  $\text{CS}_4^{2-}$  ligand a strong infrared absorption at  $980\text{ cm}^{-1}$  is attributed to the C=S asymmetric stretching vibration [131].  $(\text{PPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$  shows three very strong absorption bands at  $1030$ ,  $965$  and  $910\text{ cm}^{-1}$  and a medium intensity band at  $850\text{ cm}^{-1}$ . The  $1030$  and  $965\text{ cm}^{-1}$  bands could be tentatively assigned to the symmetric and asymmetric  $\nu(\text{C=S})$  vibrations, respectively. Coucouvanis and Fackler [179] have reported the synthesis of the same anion using a different preparative route and have assigned a strong band near  $1035\text{ cm}^{-1}$  to C=S stretch. Their reported spectrum of the said complex shows all the four absorptions in the  $1035\text{-}850\text{ cm}^{-1}$  range, but no other assignments have been made. We have assigned the low energy vibrations at  $340$  and  $309\text{ cm}^{-1}$  to  $\nu(\text{Ni-S})$ . As discussed earlier  $\text{CS}_4^{2-}$  should be a better coordinating bidentate ligand than  $\text{S}_4^{2-}$  ligand, since, in the latter case the M-S<sub>4</sub> ring is not planar. Consequently Ni-S bond in  $\text{CS}_4^{2-}$  coordinated

complex should have stronger  $\pi$ -character than that of  $S_4^{2-}$  coordinated complex. The other important bands which appear in the  $500\text{--}400\text{ cm}^{-1}$  range could be due to  $\nu(\text{S--S})$  and deformation vibrations of the entire  $CS_4^{2-}$  group. Proper assignments for these bands are not possible with the infrared data alone.

The corresponding palladium compound  $(Et_4N)_2[Pd(CS_4)_2]$  shows similar four vibrations in the range  $1050\text{--}850\text{ cm}^{-1}$ . The  $\nu(Pd\text{--}S)$  appears at  $330$  and  $305\text{ cm}^{-1}$ . It is interesting to note here that the counter cation used in this case is tetraethylammonium instead of tetraphenylphosphonium. Hence an additional band at  $510\text{ cm}^{-1}$  can be located in this compound. Although,  $\nu(\text{S--S})$  vibration generally appears in this region [2], in these systems no vibration appearing in this region is pure in nature and the occurrence of all these bands within a very narrow range with medium to weak intensity makes any speculative assignment difficult.

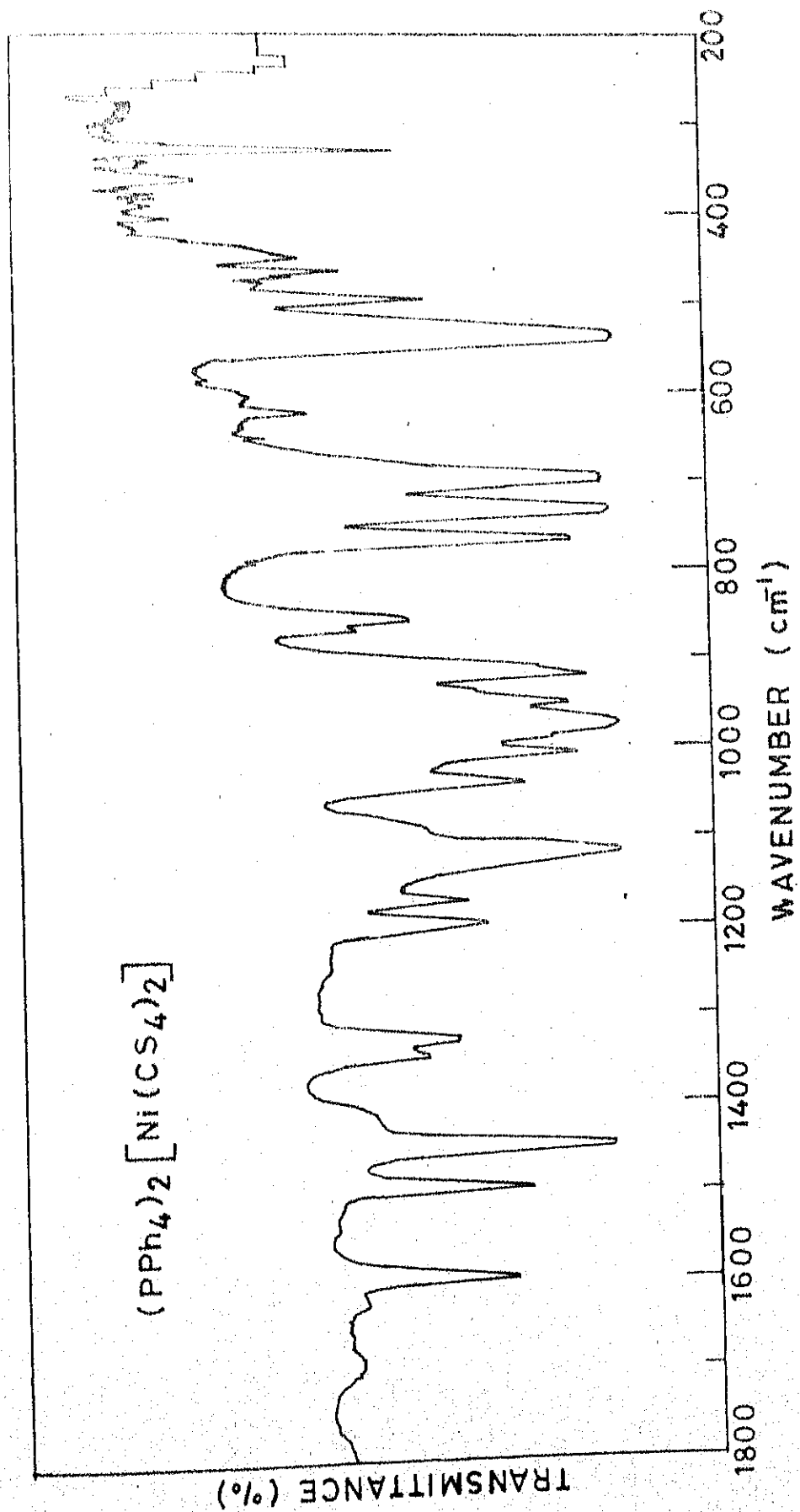
For the substituted  $CS_4^{2-}$  complexes of the general formula  $[Ni(L\text{--}L)(CS_4)]$  ( $L\text{--}L = o\text{-phen, bipy}$ ) the pattern of the infrared spectra are similar to those of the anionic bisperthiocarbonato complexes. For the *o*-phenanthroline derivative a band arising at  $850\text{ cm}^{-1}$  due to  $C=S$  vibration is masked by the strong absorption of the coordinated *o*-phenanthroline. The  $\nu(Ni\text{--}S)$  could be assigned to the weak bands at  $335$  and  $320\text{ cm}^{-1}$ . For the corresponding bipyridyl analog  $\nu(Ni\text{--}S)$  vibrations appear at  $340$  and  $310\text{ cm}^{-1}$ .

The insertion reaction of COS with the polysulfido complexes gives the compounds  $(PPh_4)_2[Ni(COS_3)_2]$  and  $(Et_4N)_2[Pd(COS_3)_2]$ . The two possible structures of the  $M-COS_3$  fragment are as shown below:



No  $\nu(C=O)$  vibration can be seen in the infrared spectra of these complexes, thus, ruling out the possibility of structure I. If the second structure is assumed then the effect of the oxygen incorporated into the ring should be seen in the infrared spectrum. In the spectrum of  $(PPh_4)_2[Ni(COS_3)_2]$  (Fig. 4.2.15) an extra band appears at  $1235\text{ cm}^{-1}$  which is absent in the spectrum of  $(PPh_4)_2[Ni(CS_4)_2]$ . Similarly, an extra band appears at  $1095\text{ cm}^{-1}$  in the spectrum of  $(Et_4N)_2[Pd(COS_3)_2]$  (Fig. 4.2.16). The origin of these bands can be tentatively assigned to the C-O group associated in the ring  $M-COS_3$ . Another interesting difference in the spectrum of the nickel complex is a set of vibrations appearing around  $600\text{ cm}^{-1}$  which are absent in the  $CS_4^{2-}$  complex. The  $\nu(Ni-S)$  is tentatively assigned to a band at  $312\text{ cm}^{-1}$ . The corresponding palladium analog shows  $\nu(Pd-S)$  at  $310\text{ cm}^{-1}$ .





INFRARED SPECTRUM

FIG. 4.2.11

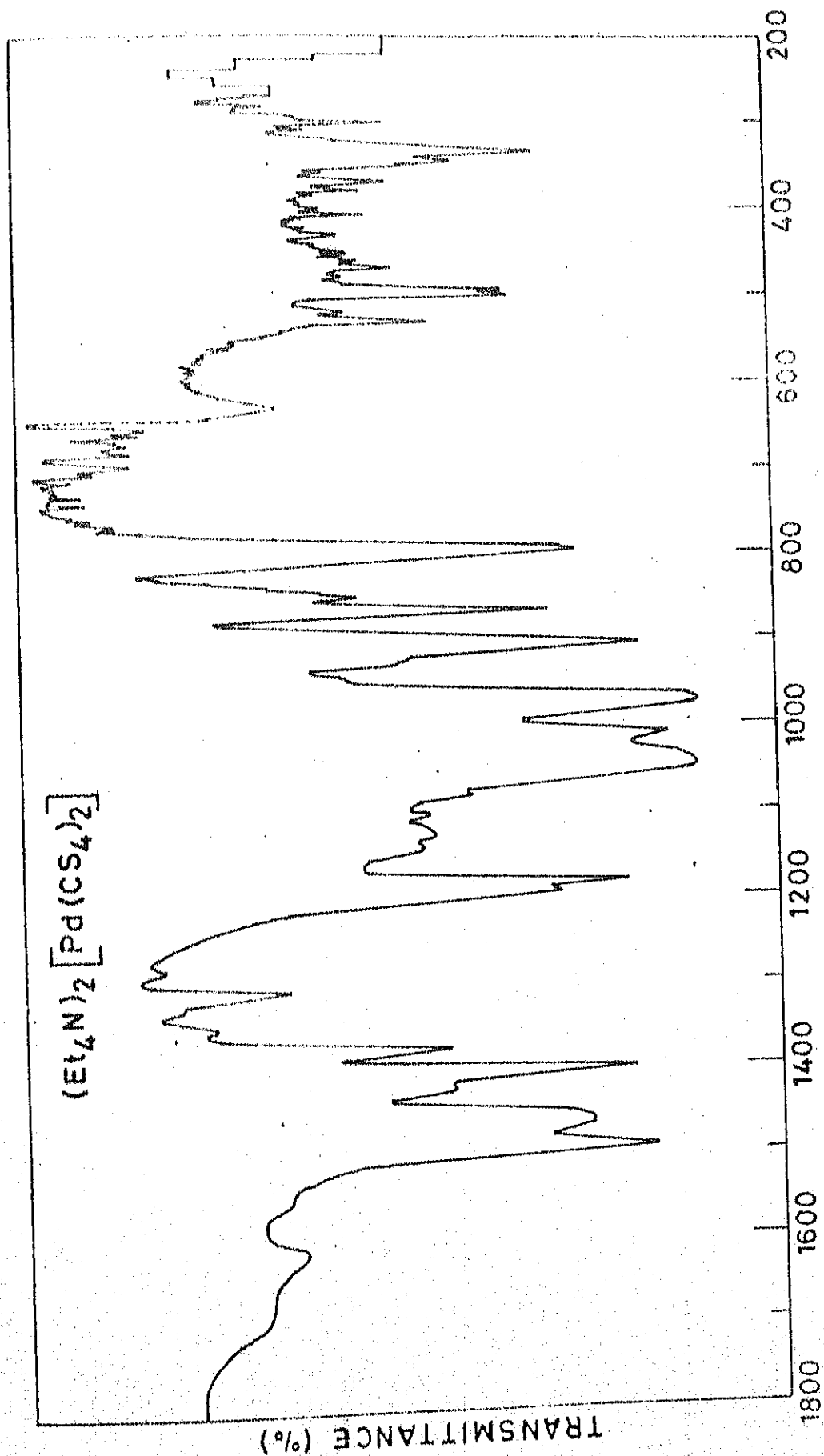
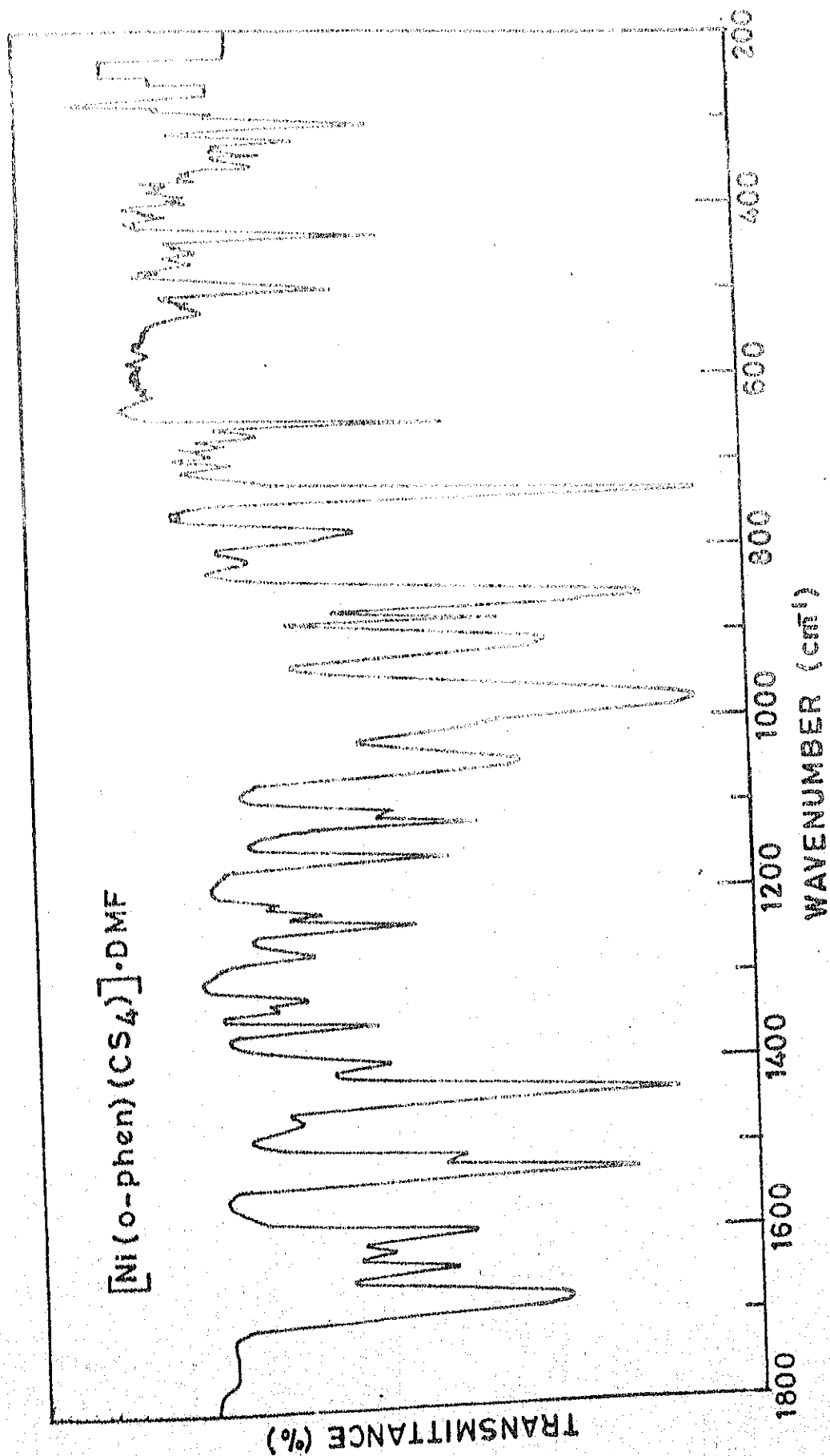


FIG. 4.2.12



INFRARED SPECTRUM

FIG. 4.2.13

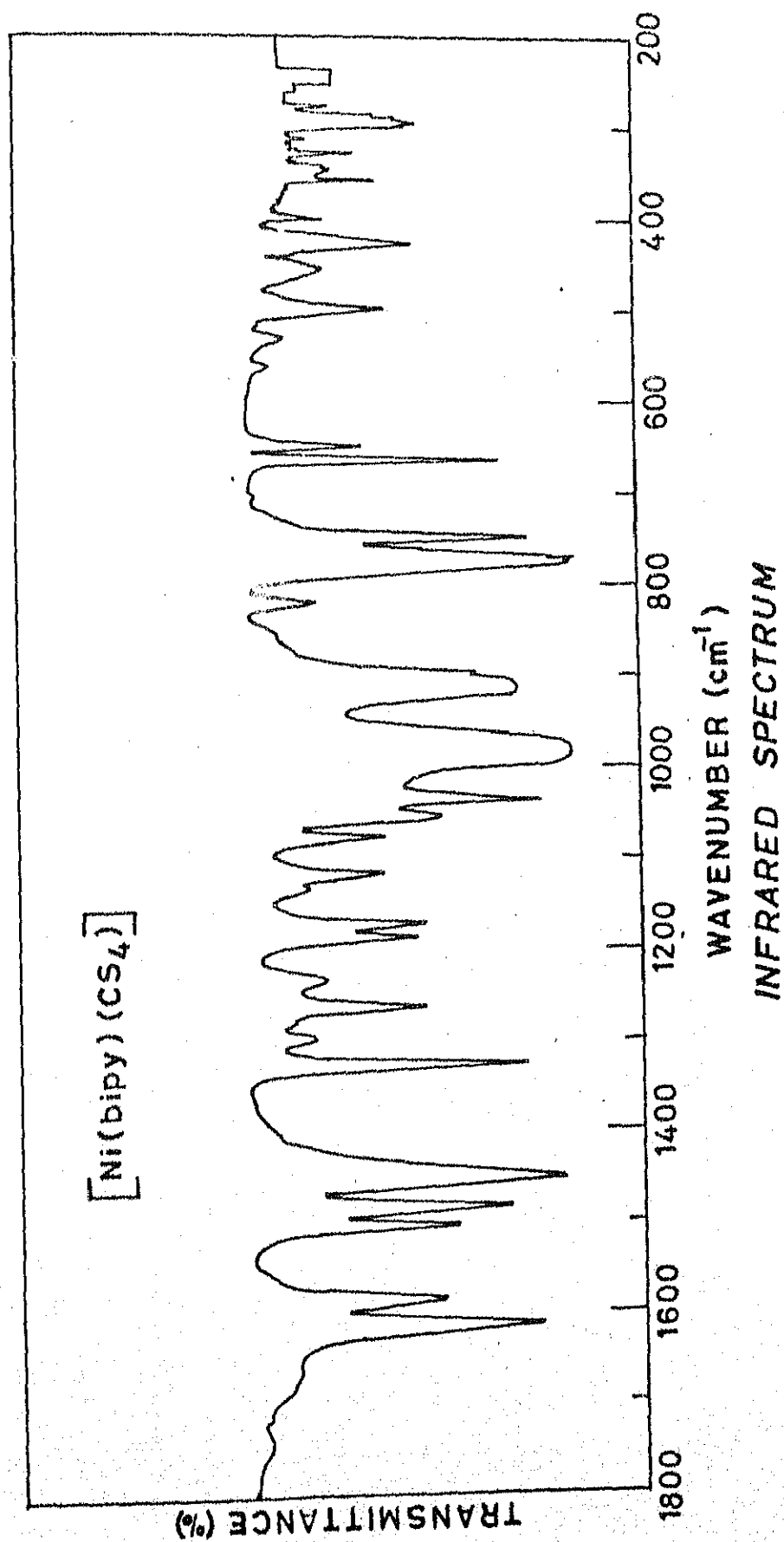


FIG.4.2.14

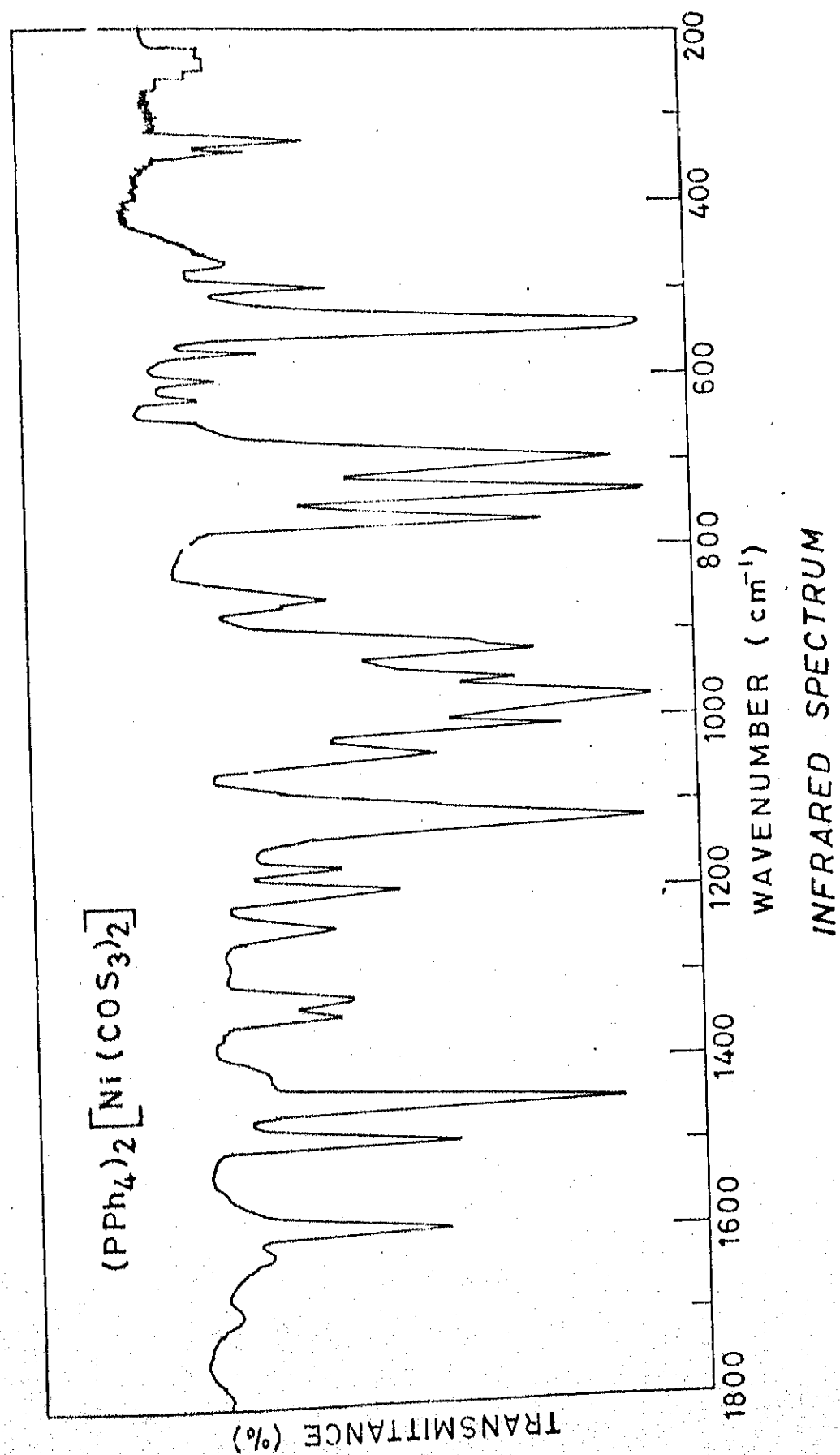


FIG. 4.2.15

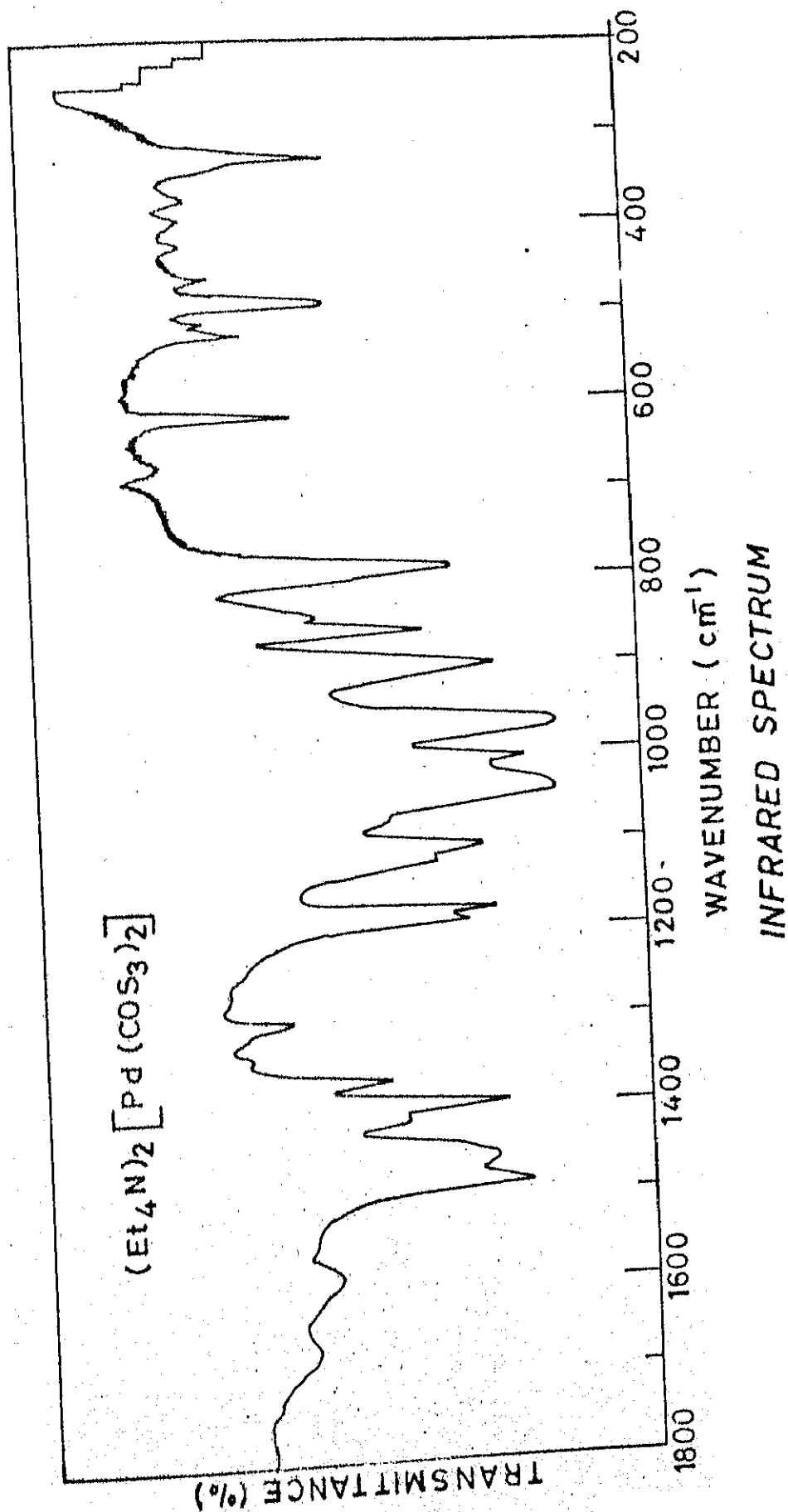


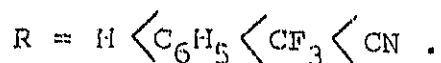
FIG. 4.2.16

Table 4.2.2 Infrared spectral data of  $\text{CS}_4^{2-}$  and  $\text{COS}_3^{2-}$  Complexes

Complex	$\nu(\text{C}=\text{S})$ ( $\text{cm}^{-1}$ )	$\nu(\text{M}-\text{S})$ ( $\text{cm}^{-1}$ )	Other important frequencies ( $\text{cm}^{-1}$ )
$(\text{PPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$	1030, 965, 910, 850	340, 309	610, 474, 442, 428
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{CS}_4)_2]$	1048, 960, 895, 855	330, 305	620, 510, 475, 445
$[\text{Ni}(\text{o-phen})(\text{CS}_4)] \cdot \text{DMF}$	1038, 970, 900	335, 320	1668 ( $\nu_{\text{CO}}$ ); 500, 480, 435, 290 ( $\nu_{\text{NiN}}$ )
$\text{Ni}(\text{bipy})(\text{CS}_4)$	1040, 970, 900	340, 310	480, 435, 405, 380, 280 ( $\nu_{\text{NiN}}$ )
$(\text{PPh}_4)_2[\text{Ni}(\text{COS}_3)_2]$	1030, 968, 910, 850	312	1235, 585, 555, 480, 450
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{COS}_3)_2]$	1030, 960, 890, 850	310	1095, 610, 515, 470

The outcome of the interaction of the polysulfido complexes with substituted acetylenes is the isolation of complexes containing dithiolene ligands. A detailed normal coordinate analysis of nickel dithiolene complexes has been reported in the literature [205]. One interesting aspect in our synthesis is the concomitant oxidation of dinegative starting materials to mononegative dithiolene complexes. In this series  $[M(S_2C_2R_2)_2]^{n-}$  ( $n = 0, -1, -2$ ) the perturbed C=C stretching frequency is a rough measure of the C=C bond strength as it couples very little with other modes. An increase in the C=C stretching frequency can be seen when the formal oxidation state of the metal decreases from +4 to +3 and then to +2. The calculation on C-S and M-S stretching modes show their coupling with other modes. Therefore, a precise change in these bonds should not be discussed in terms of stretching frequencies. In the mononegative complex ion the highest occupied molecular orbital ( $b_{2g}$ ) is bonding in nature with respect to the C=C but antibonding with respect to the C-S and M-S bonds. The addition of an electron to this orbital is expected to strengthen C=C and weaken C-S and M-S bonds. The changes in force constants and charge densities are available for a series of mononegative complexes [205]. The dithiolenes used are of the type  $S_2C_2R_2^{2-}$ , where  $R = H, C_6H_5, CF_3$  and  $CN$ . The electron density of the extra electron on the nickel atom increase in the order





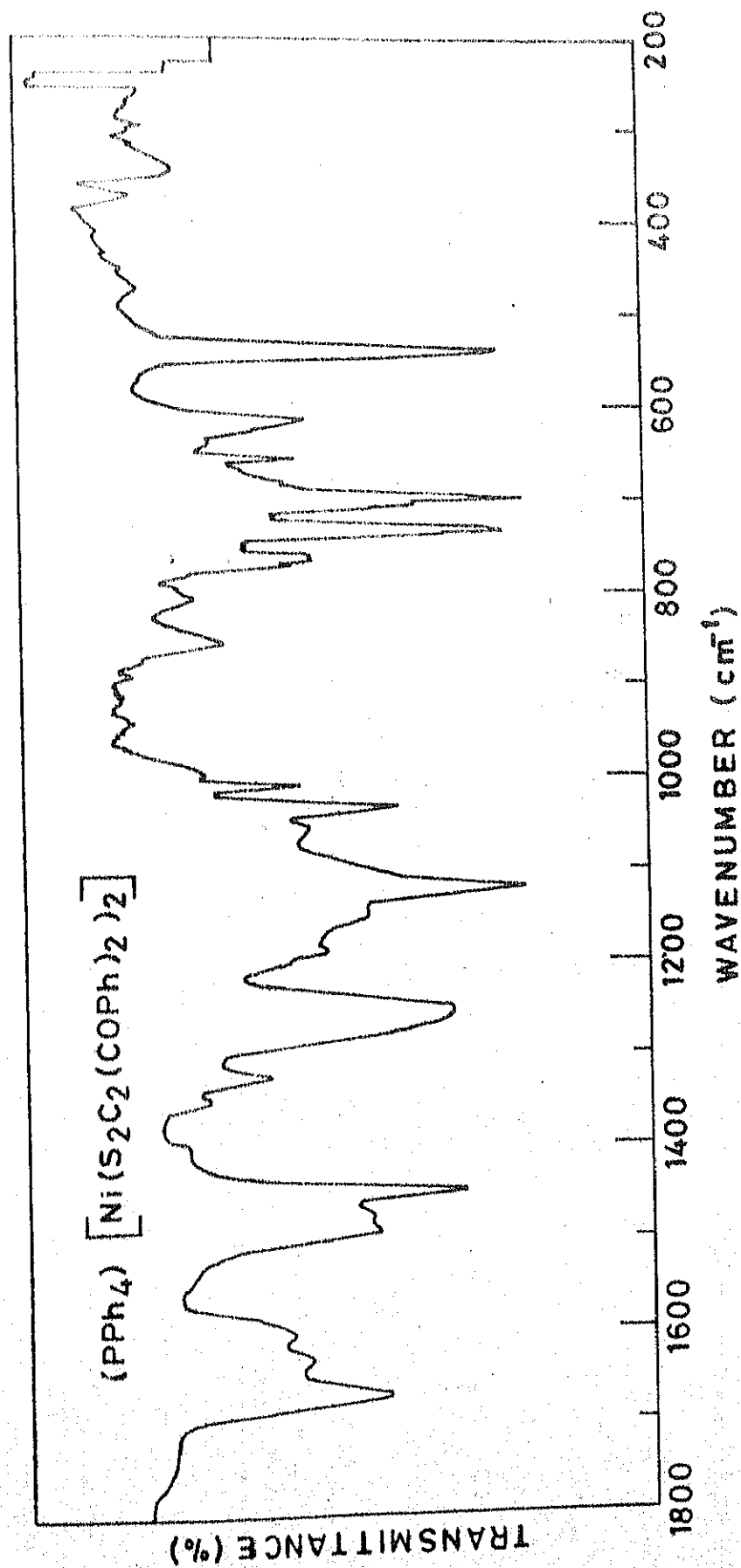
Thus, for  $S_2C_2H_2^{2-}$  the electron density of the HOMO contains 6% metal character, whereas for  $S_2C_2(CN)_2^{2-}$  38% of the electron density has been calculated to reside on the metal orbital. For this cyano derivative esr study shows this contribution to be 42% [206-207]. The orbital accepting the odd electron is an antibonding combination of a ligand and the metal  $d_{xz}$  orbital. When  $R = H$  the ligand  $\pi$ -orbital lies energetically much higher than the metal  $d_{xz}$  orbital. As a result the antibonding orbital has little  $d_{xz}$  character. If  $H$  is replaced by a better electron acceptor, the  $\pi$ -orbital is stabilized and becomes closer to the  $d_{xz}$  orbital. Thus, in this group of ligands it can be assumed that when  $R$  is a better  $\pi$ -acceptor, the mononegative complex contains the metal in the +3 formal oxidation state. On the other hand, if the unpaired electron resides in an orbital predominantly ligand in character, the formal oxidation state of the metal ion can be considered as +2 only (vide supra).

We have used two acetylenes both having electron withdrawing substituents. The infrared spectra of the synthesized  $M(III)$  dithiolene complexes are reproduced in Figs. 4.2.17 - 4.2.20 and the important band positions are given in Table 4.2.3.

As discussed earlier the  $C \equiv C$  stretching frequency is a rough measure of the  $C \equiv C$  bond strength. In a series of

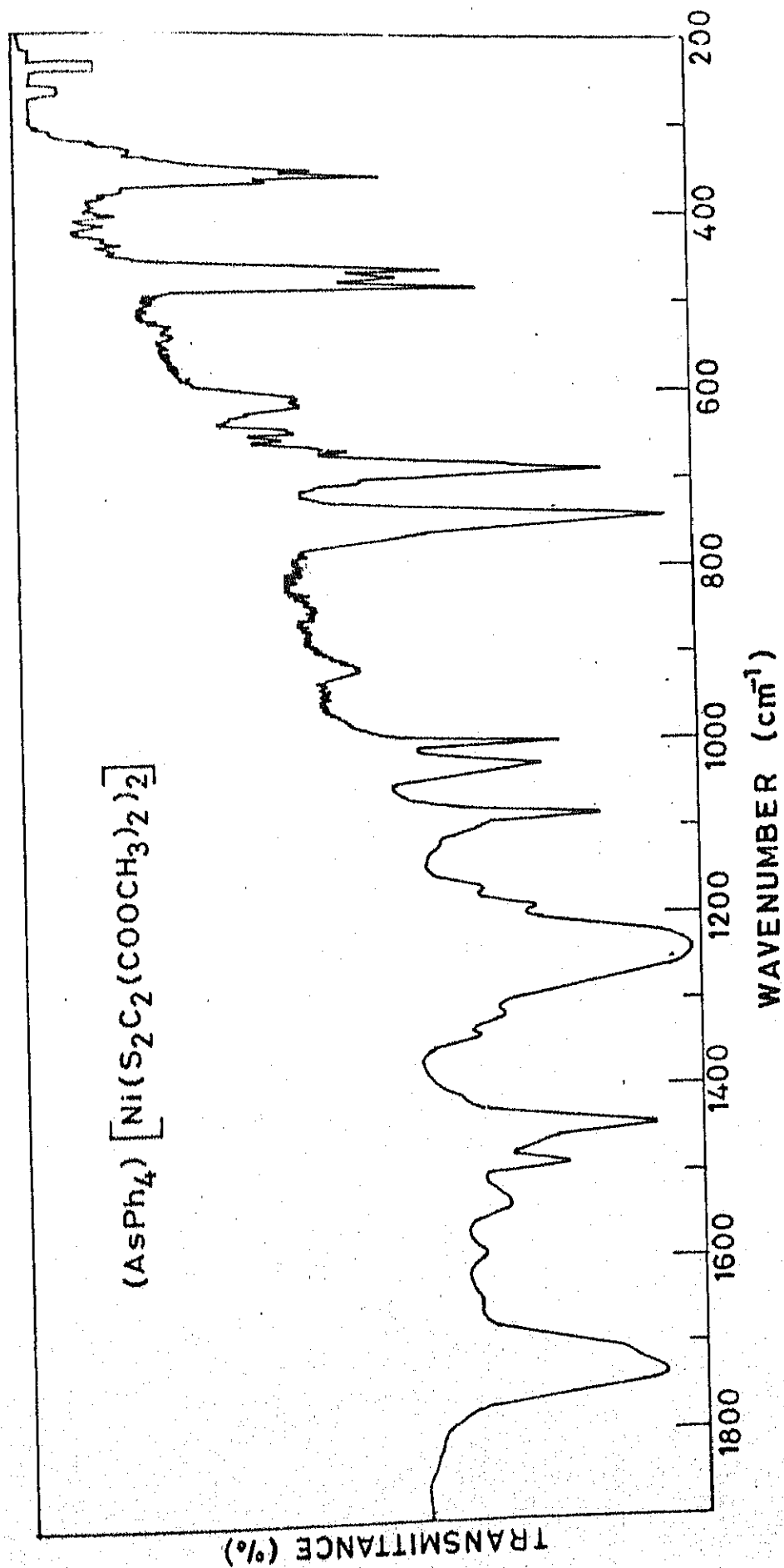
mononegative anions the other electronic factors which affect the C=C stretching frequency would be mainly dependent on the nature of the substituent group on the carbon atoms. When  $R = \text{Ph}$  a considerable reduction of  $\nu(\text{C}=\text{C})$  is found for all compounds reported here. Contrary to this, when  $R = \text{COOCH}_3$ ,  $\nu(\text{C}=\text{C})$  appears  $\sim 60 \text{ cm}^{-1}$  higher than that found in COPh substituted compounds. It is difficult to locate the  $\nu(\text{C}\equiv\text{C})$  vibrations of the starting acetylenes, used in this work because this symmetric vibration is very weak in nature. Apparently a lower  $\nu(\text{C}=\text{C})$  frequency in the -COPh substituted dithiolene mononegative complex indicates a better  $\pi$ -electron delocalization than that in the -COOCH<sub>3</sub> substituted dithiolene complex. We did not isolate the corresponding dinegative complex ion to make a comparison of the difference in  $\nu(\text{C}=\text{C})$  in two different oxidation states of the metal. It is understood that for the corresponding dinegative ion this stretching vibration should shift to higher frequency. We have isolated a neutral diamagnetic substituted complex  $[\text{Pd}(\text{o-phen})(\text{S}_2\text{C}_2(\text{COPh})_2)]$  where the  $\nu(\text{C}=\text{C})$  vibration is masked by the  $\nu(\text{C}=\text{C})$  vibration arising from the coordinated o-phenanthroline (Fig. 4.2.21). Yet, the appearance of this band around  $1490 \text{ cm}^{-1}$  does suggest an upward shift of this band compared to the mononegative ion,  $[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^-$ . However, this  $25 \text{ cm}^{-1}$  increase is not much compared to other reported shifts from mononegative to dinegative ions where, on an average, the shift is  $\sim 55 \text{ cm}^{-1}$  [205]. In our neutral complex the  $\nu(\text{Pd-N})$  does not show any dramatic

shift compared to that of other substituted o-phenanthroline complexes (vide infra). Thus, if the shift in this vibration frequency is an indication of extra  $\pi$ -electron density drift between metal-o-phenanthroline system, then the less shift in this compound suggests less participation of ligand  $\pi$ -electron density in the highest occupied molecular orbital. It is argued that the HOMO for dinegative ion is predominantly comprised of metal d-character [168] and as the electrons are removed from this orbital, the contribution of more ligand  $\pi$ -character comes in for this MO (vide supra). Thus, for the complexes of  $S_2C_2(COOCH_3)_2^{2-}$  which has a better  $\pi$ -accepting substituent, it can be anticipated that the electron density in the HOMO should have more metal character. The appearance of  $\nu(C=C)$  for  $[M(S_2C_2(COOCH_3)_2)]^-$  ( $M = Ni, Pd$ ) at  $1522\text{ cm}^{-1}$  is so far the highest value observed for this class of compounds. With this observation one can presume that in this case the  $\pi$ -orbital is stabilized more and becomes closer to the  $d_{xz}$  orbital causing more metal character of the electron density in the HOMO. As discussed earlier it is difficult to guess anything about the nature of bond order of  $\nu(M-S)$  by infrared data to augment the arguments presented in this context, however, esr spectral data supports these view points (vide infra). The important assignments of other vibrations for this class of compounds have been made by comparing the reported data for similar complexes and are listed in Table 4.2.3.



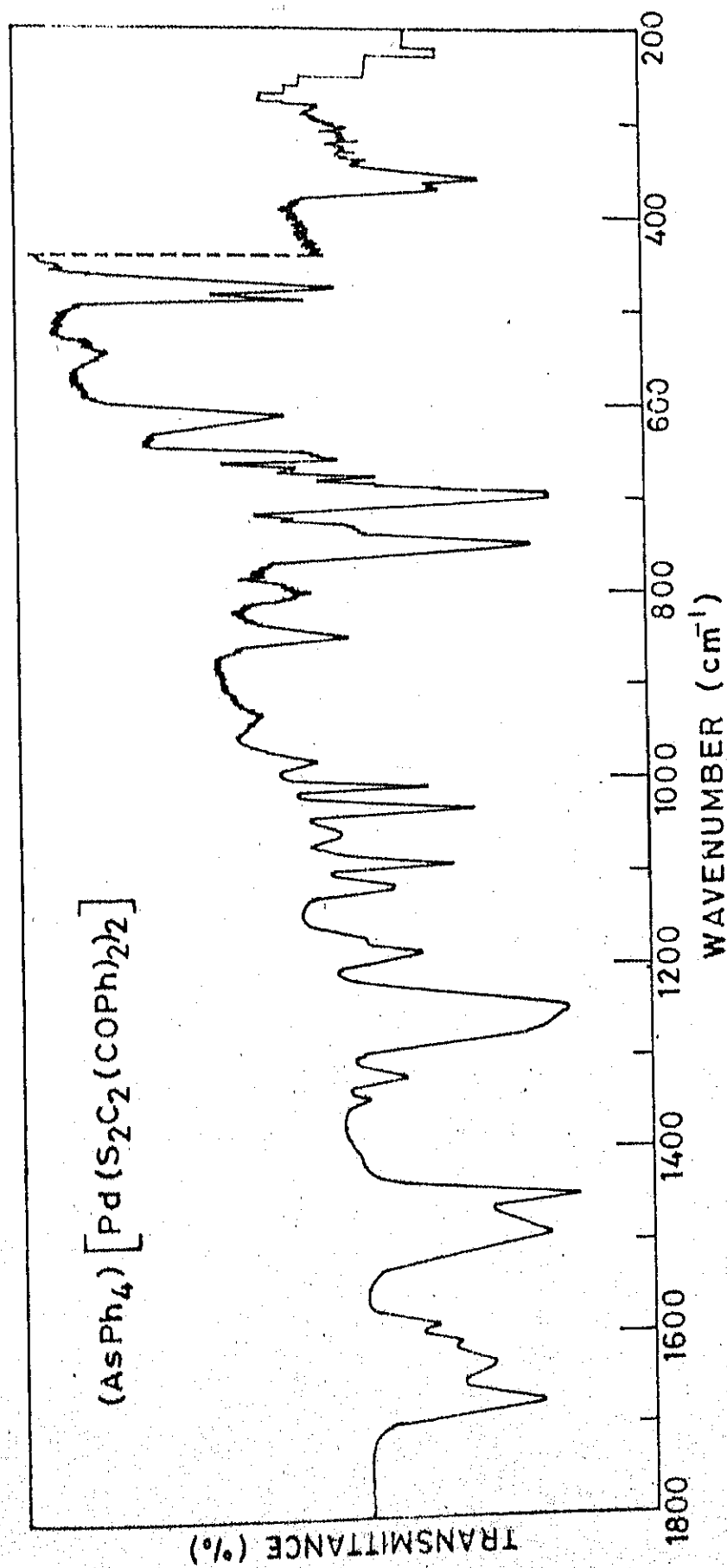
INFRARED SPECTRUM

FIG. 4.2.17



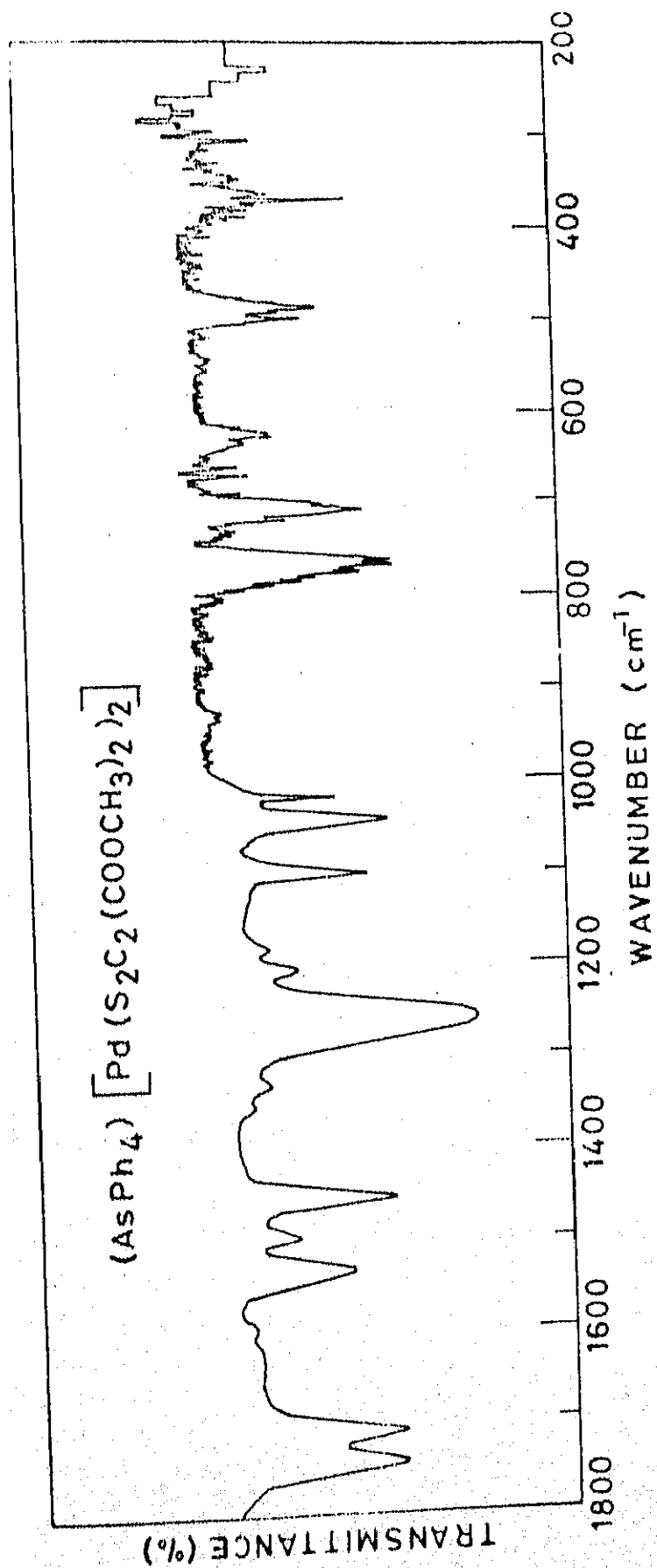
WAVENUMBER (cm⁻¹)  
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FIG. 4.2.18



INFRARED SPECTRUM

FIG. 4.2.19



INFRARED SPECTRUM

FIG. 4.2.20

Table 4.2.3 Infrared spectral data of dithiolene complexes

Complex	$\nu(\text{C}=\text{C})$ ( $\text{cm}^{-1}$ )	Other important frequencies ( $\text{cm}^{-1}$ )			Reference
		1	2	3	
$(\text{PPh}_4)[\text{Ni}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	1465		1660 ( $\nu_{\text{C}=\text{O}}$ ), 445, 350, 330		This work
$(\text{AsPh}_4)[\text{Ni}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]$	1522		1725 ( $\nu_{\text{C}=\text{O}}$ ), 600		This work
$(\text{Et}_4\text{N})[\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2]$	1435		840 ( $\nu_{\text{C}-\text{S}}$ + ring def.); 790 ( $\nu_{\text{C}-\text{S}}$ ); 705, 694 (ring def.); 411.5, 385 ( $\nu_{\text{Ni}-\text{S}}$ )		205
$(\text{Et}_4\text{N})[\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]$	1485		918, 847 ( $\nu_{\text{C}-\text{S}}$ ); 449, 415 ( $\nu_{\text{Ni}-\text{S}}$ )		205
$(\text{Et}_4\text{N})[\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]$	1475		960, 870 ( $\nu_{\text{C}-\text{S}}$ ); 465, 406 ( $\nu_{\text{Ni}-\text{S}}$ + ring def.); 428 ( $\nu_{\text{Ni}-\text{S}}$ )		205
$(\text{Et}_4\text{N})[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$	1435		2195 ( $\nu_{\text{C}\equiv\text{N}}$ ); 1170, 1055 ( $\nu_{\text{C}-\text{S}}$ + $\nu_{\text{C}-\text{C}}$ ); 865 ( $\nu_{\text{C}-\text{S}}$ ); 457, 365, 357 ( $\nu_{\text{Ni}-\text{S}}$ + ring def.)		205
$(\text{AsPh}_4)[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	1465		1662 ( $\nu_{\text{C}=\text{O}}$ ), 605		This work
$(\text{AsPh}_4)[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]$	1522		1722, 1698 ( $\nu_{\text{C}=\text{O}}$ ), 602		This work
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	1450		1662 ( $\nu_{\text{C}=\text{O}}$ ), 530, 330		This work

165  
65

...contd.



Table 4.2.3 (contd.)

1	2	3	4
$(\text{AsPh}_4)_2[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$	1510	1720, 1696 ( $\nu_{\text{C=O}}$ ), 604	This work
$(\text{Et}_4\text{N})_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	1450	1660 ( $\nu_{\text{C=O}}$ ), 550, 430, 360, 320	This work
$(\text{AsPh}_4)_2[\text{Pt}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$	1515	1715, 1695 ( $\nu_{\text{C=O}}$ ), 600	This work
$[\text{Pd}(\text{o-phen})(\text{S}_2\text{C}_2(\text{COPh})_2)]$	1490	1665 ( $\nu_{\text{C=O}}$ ), 600, 525, 485, 430, 360	This work

For the tris-dithiolene complexes of Pd(IV) and Pt(IV) the spectra are reproduced in Figs. 4.2.22 - 4.2.25. Assignments of the important vibrations have been made as per the discussion mentioned above, and these are tabulated in Table 4.2.3. It is known that higher the coordination number lower is the stretching frequency and higher the oxidation state higher is the stretching frequency. For this series of complexes the coordination number is enhanced to six and the oxidation state is also increased to +4. The degree of these two counter effects is difficult to assign and  $\nu(\text{M-S})$  vibrations are often strongly coupled with  $\pi$ -ring vibrations. For these reasons along with the fact that the actual structural information about these complexes are not known, a serious discussion in this regard is not possible.

The infrared spectrum of  $[\text{Ni}(\text{o-phen})(\text{S}_3\text{O}_2)]$  is reproduced in Fig. 4.2.26. The coordinated  $\text{S}_3\text{O}_2^{2-}$  should give characteristic  $\nu_{\text{as}}(\text{SO}_2)$  and  $\nu_{\text{s}}(\text{SO}_2)$  vibrations along with  $\nu_{\text{as}}(\text{S-S}_2)$  and  $\delta(\text{SO}_2)$ . For the chelating bidentate sulfate coordination in  $[\text{Pd}(\text{o-phen})(\text{SO}_4)]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SO}_4)]$  the  $\nu_{\text{as}}(\text{SO}_2)$  appears around  $1250 \text{ cm}^{-1}$  and the corresponding  $\nu_{\text{s}}(\text{SO}_2)$  appears in the range  $955-920 \text{ cm}^{-1}$  [209,209]. The  $\nu_{\text{as}}(\text{SO}_2)$  for the only reported dithiosulfato complex  $(\text{PPh}_4)_2[(\text{S}_2)\text{OMoS}_2\text{MoO}(\text{S}_3\text{O}_2)]$  appears at  $1255 \text{ cm}^{-1}$  [112]. The symmetric stretching frequency for this compound has not been reported probably because it is masked by the very strong absorption due to  $\nu(\text{Mo-O})$  occurring

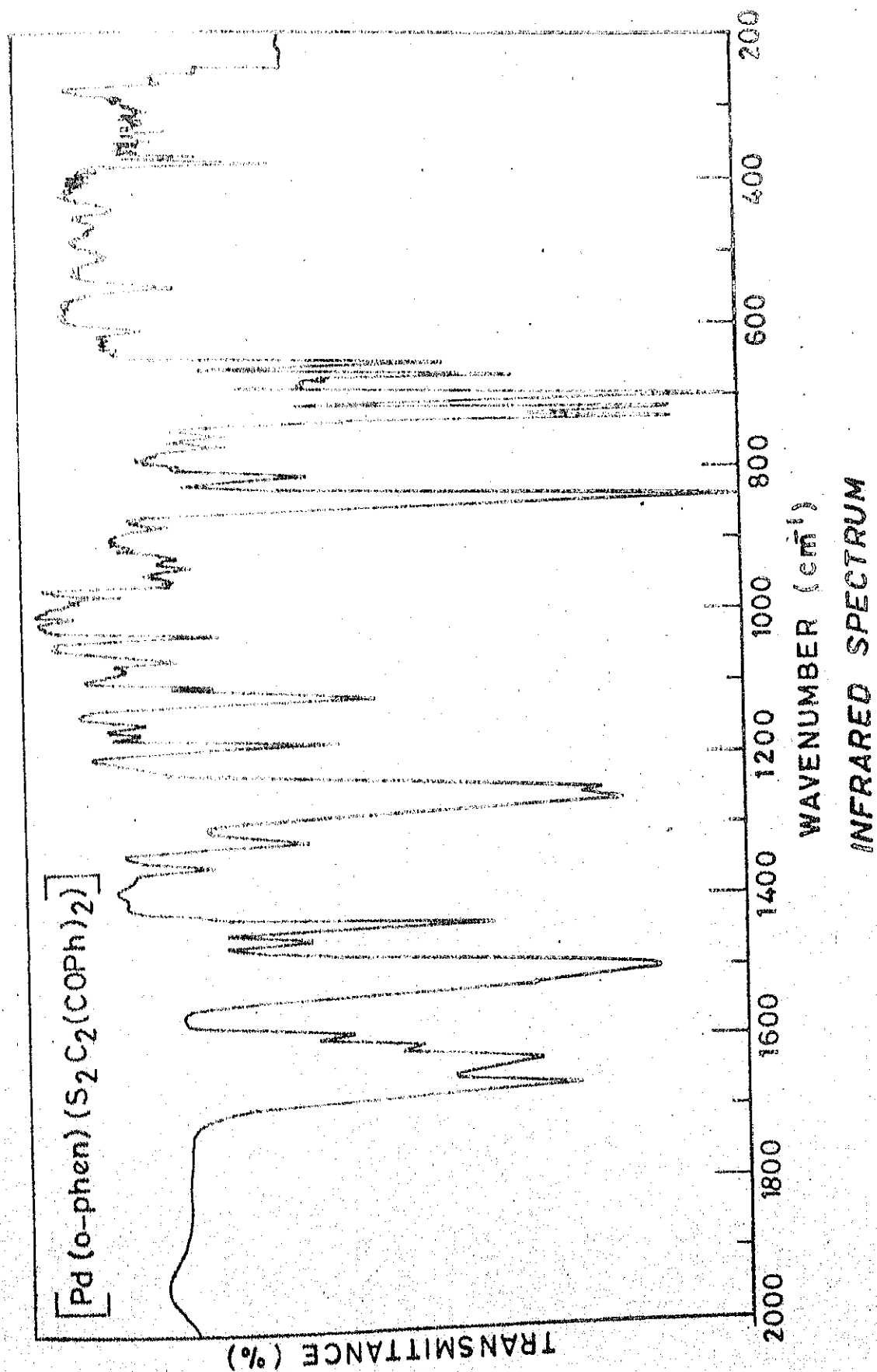


FIG. 4.2.21

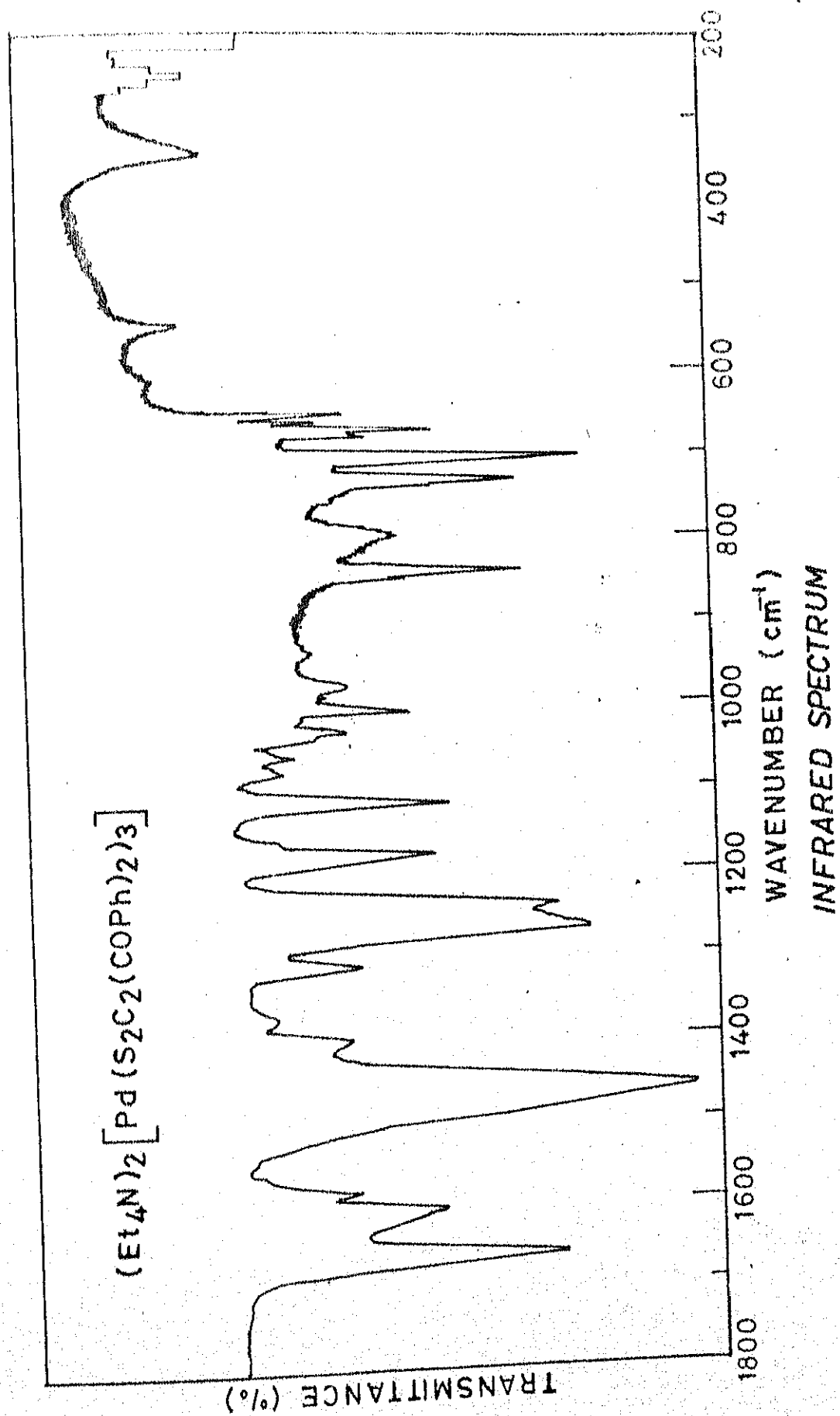


FIG. 4.2.22

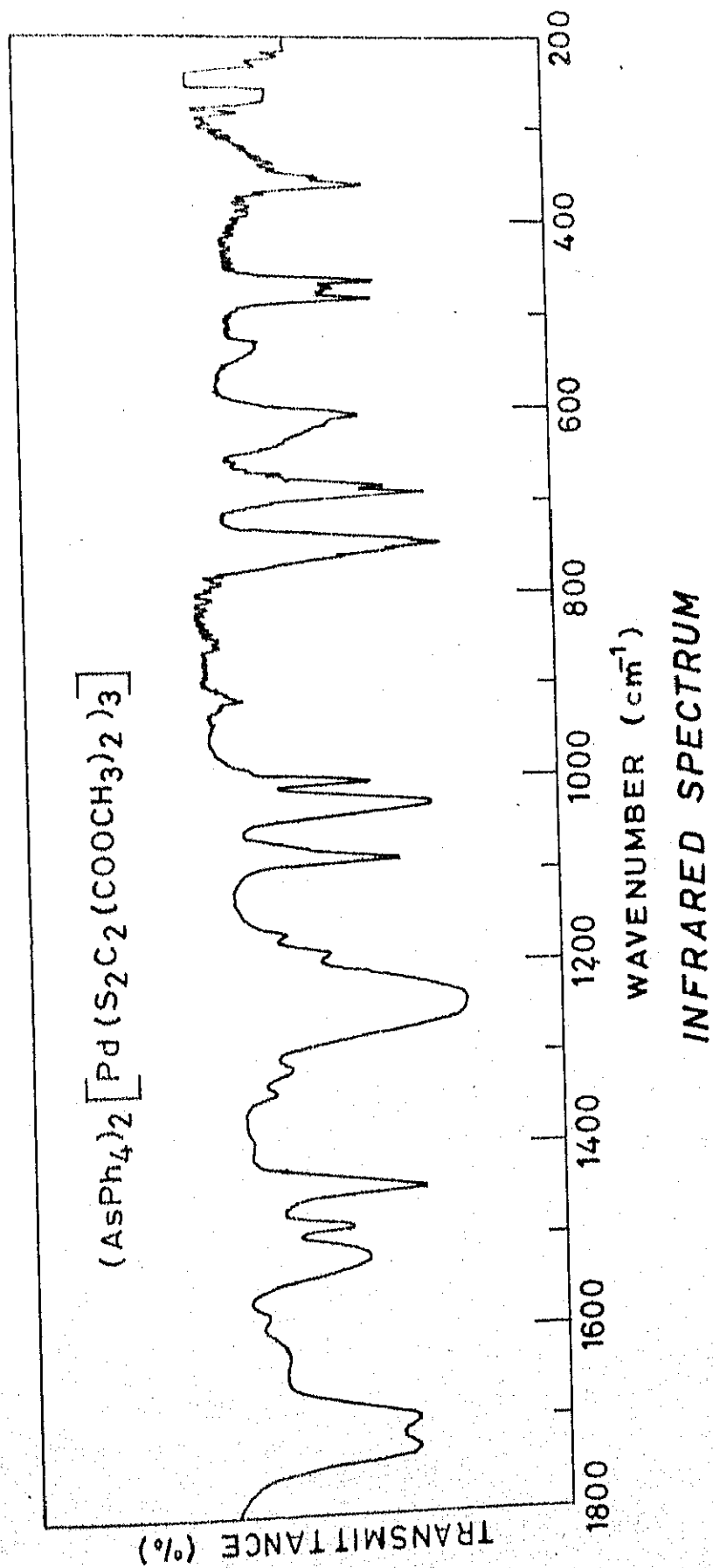
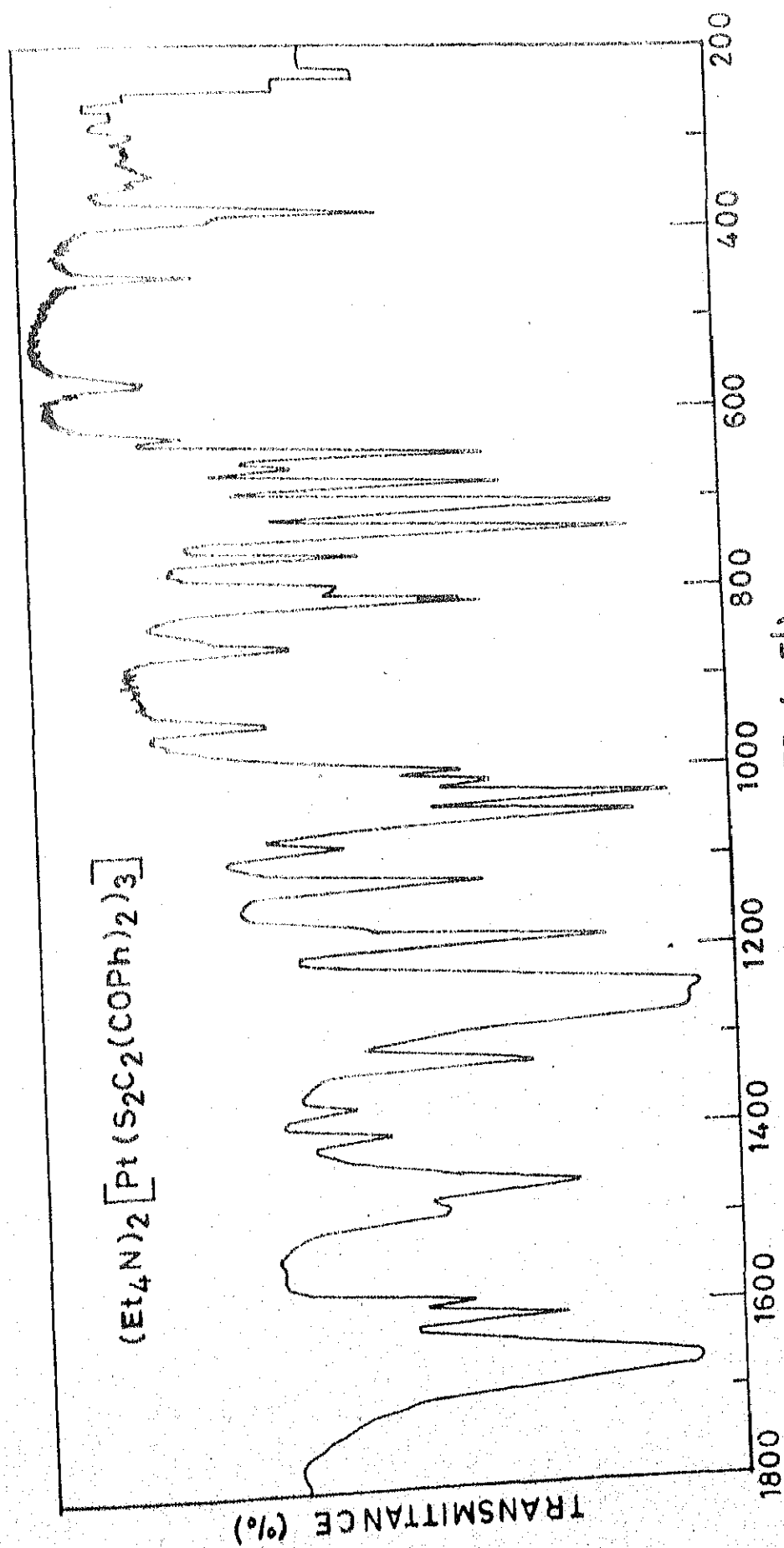


FIG. 4.2.23



INFRARED SPECTRUM

FIG. 4.2.24

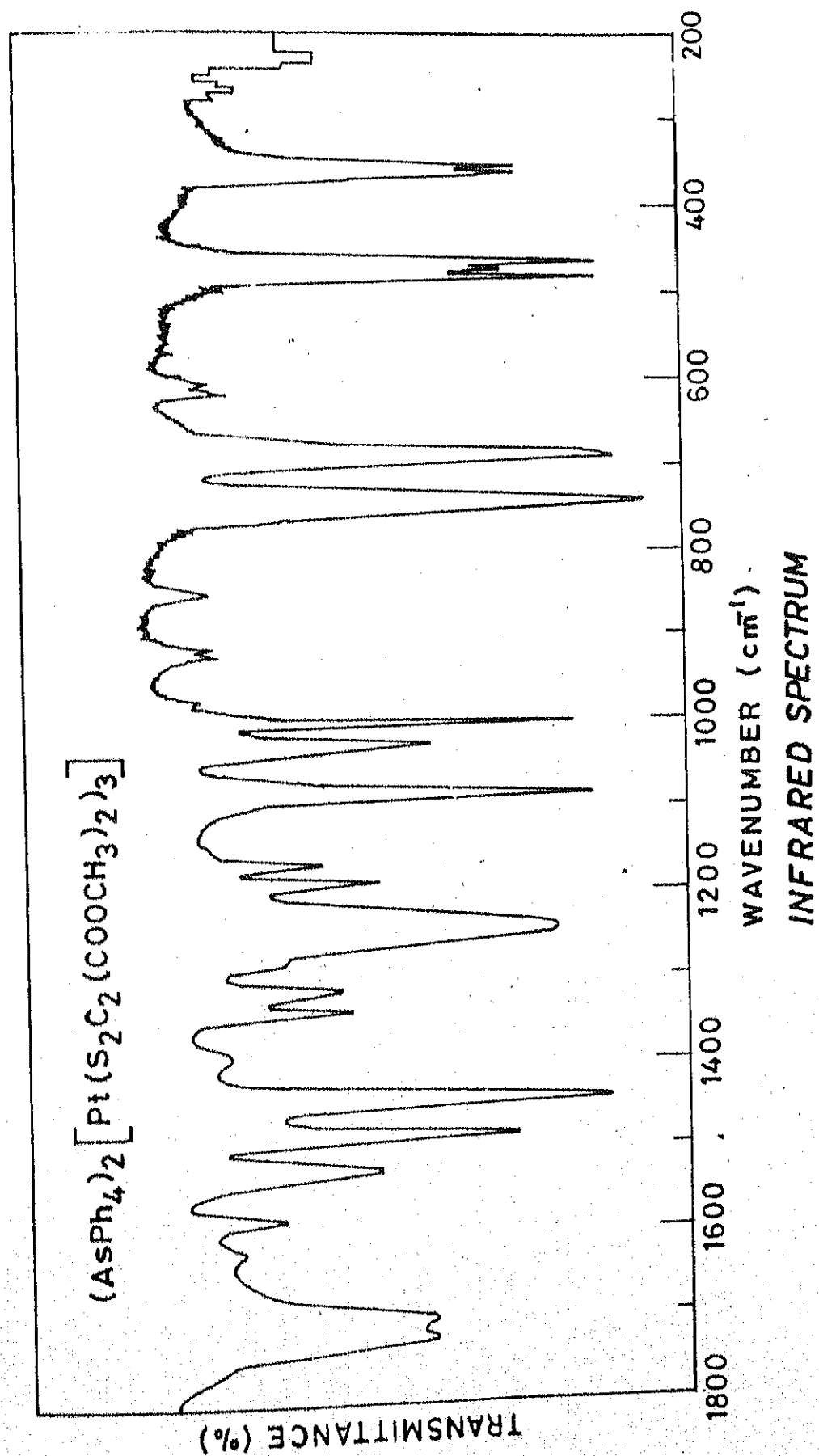


FIG. 4.2.25

at  $955\text{ cm}^{-1}$ . In our nickel complex a very strong absorption appearing around  $1230\text{ cm}^{-1}$  is assigned to  $\nu_{\text{as}}(\text{SO}_2)$ . The corresponding symmetric vibration appears around  $985\text{ cm}^{-1}$ . It is difficult to assign the  $\nu_{\text{as}}(\text{S-S}_2)$  and  $\delta(\text{SO}_2)$  modes of vibration as they appear in the same frequency region. However, a strong band at  $605\text{ cm}^{-1}$  is tentatively assigned to  $\delta(\text{SO}_2)$ . The corresponding bipyridyl analog also gives a similar spectrum.

#### Other Ligand Vibrations

The infrared spectrum of the cyanosubstituted complex,  $(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$  (Fig. 4.2.6) shows  $\nu(\text{CN})$  at  $2070$  and  $2110\text{ cm}^{-1}$  which are lower than the  $\nu(\text{CN})$  of the starting tetracyanonickelate [210]. This is expected for the effective increase of back-bonding towards coordinated cyanide in this complex. The corresponding  $\nu(\text{Ni-C})$  at  $440$  and  $450\text{ cm}^{-1}$  which are higher than the  $\nu(\text{Ni-C})$  of the starting compound corroborate this.

The other colligands used in the synthesized complexes are aromatic diimines. Bipyridyl or o-phenanthroline, when attached to nickel or palladium can be readily deduced from the characteristic appearance of these ligand vibrations. The identification of M-N bond is possible since we observed a band around  $300\text{ cm}^{-1}$  which remains unchanged when the sulfur containing ligand is changed from  $\text{S}_4^{2-}$  to  $\text{CS}_4^{2-}$ . The position of these vibrations are listed in Tables 4.2.1 and 4.2.2.



#### 4.3 Magnetic Susceptibility and Electron Spin Resonance Spectra

All the complexes described in this thesis are diamagnetic in nature except the mononegative dithiolene complexes of nickel and palladium. The diamagnetism of the M(IV) (M = Pd, Pt) are expected and palladium(II) complexes are mostly square-planar which being a  $d^8$  system should be diamagnetic. Nickel is susceptible to occur in different stereochemistries in the +2 oxidation state, however, the diamagnetism of all the complexes reported here prove that the stereochemistry in all these cases is square-planar. When  $NiS_4$  chromophoric group is present, the square-planar nature is evident even from the other studies conducted by other workers [43,179,180]. Interestingly for the aromatic diimine substituted complexes, even the chromophoric group  $NiN_2S_2$  is sufficient to cause square-planar geometry and electronic spectral studies suggest that in solution this stereochemistry is retained (vide supra).

As expected, only the monoanions of nickel and palladium complexes containing dithiolene ligands are paramagnetic and have a doublet ground state. The effective magnetic moment values of these compounds are tabulated in Table 4.3.1. The values obtained are in good agreement with the reported data for similar complexes [192].

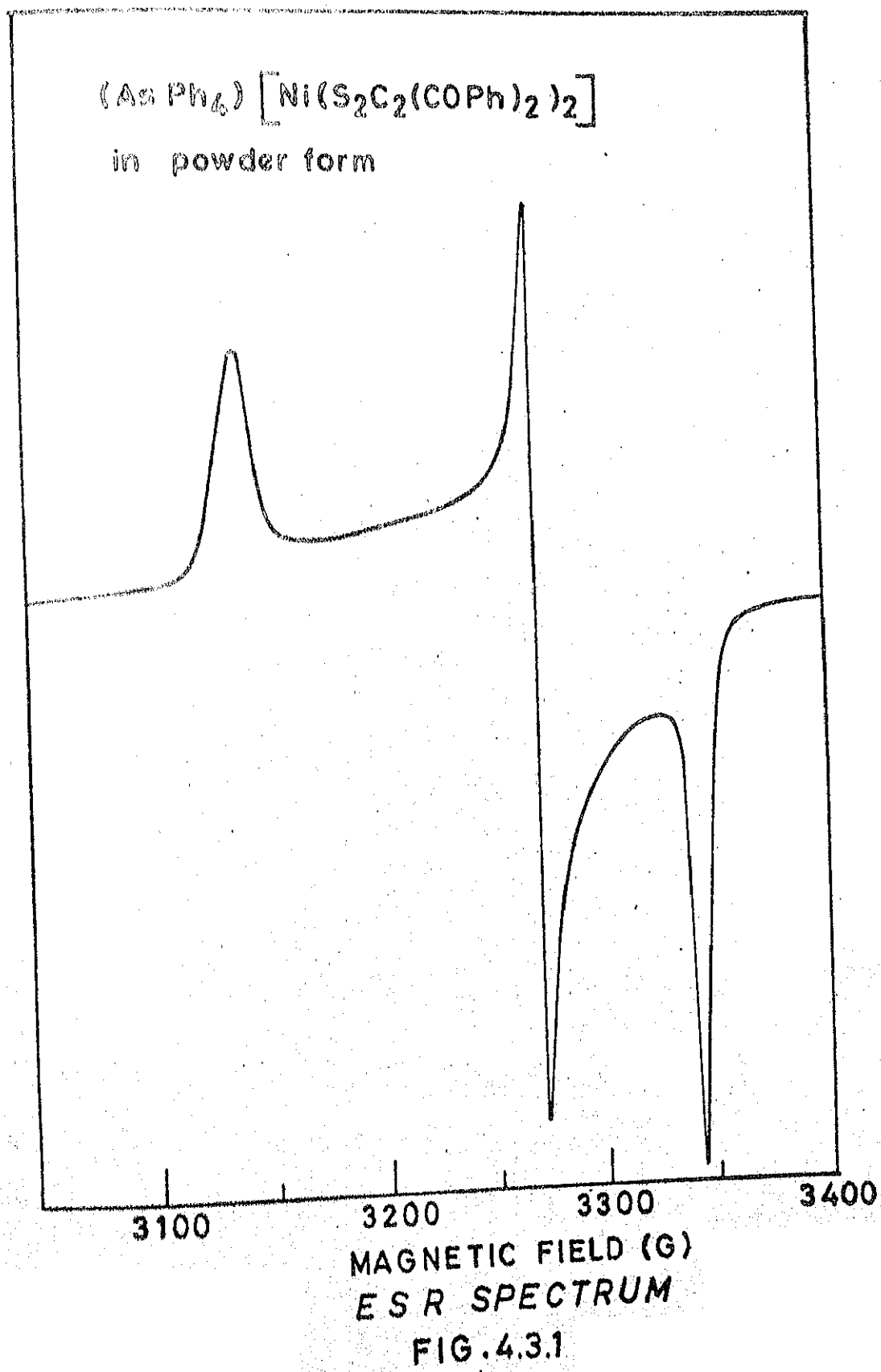
The esr spectra of the nickel and palladium monoanionic complexes are reproduced in Figs. 4.3.1 - 4.3.8. The most

noteworthy feature of these spectra is the considerable anisotropy of the  $g$  tensor which is detected even at room temperature. Another interesting feature is that nearly identical anisotropies have been found in both the nickel derivatives. However, in the palladium case,  $(AsPh_4)[Pd(S_2C_2(COPh)_2)_2]$  shows the anisotropic  $g$  tensor values similar to nickel system but for  $(AsPh_4)[Pd(S_2C_2(COOCH_3)_2)_2]$  an isotropic resonance is obtained. It is interesting to note that for the corresponding nickel complex,  $(AsPh_4)[Ni(S_2C_2(COOCH_3)_2)_2]$ , the anisotropy is also not so pronounced compared to those complexes of nickel and palladium having the other dithiolene. The complex,  $(AsPh_4)-[Ni(S_2C_2(COOCH_3)_2)_2]$ , even on diluting with KBr ( $\sim 2\%$ ) could not produce a better resolved spectrum. It is known that exchange interactions between magnetically inequivalent ions of the unit cell, if sufficiently strong will result in the averaging of the principal  $g$  values of a complex. Also we have tried to search the anisotropic  $g$  values for the complex  $(AsPh_4)-[Pd(S_2C_2(COOCH_3)_2)_2]$  by magnetically diluting it with potassium bromide, but without any success. This can be due to the accidental averaging of the principal  $g$  values in the polycrystalline salt. In Table 4.3.1 all the measured esr parameters are tabulated. The isotropic  $g$  value obtained in solution (close to solid state value) justifies our previous proposition about not getting the anisotropic  $g$  values for the said palladium complex.

Hyperfine splitting due to  $^{105}\text{Pd}$  ( $I = 5/2$ ) are readily detected as the natural abundance of this isotope is 22.23%. Unfortunately, for the corresponding nickel complexes this hyperfine interaction due to  $^{61}\text{Ni}$  ( $I = 3/2$ ) cannot be seen, because its natural abundance is only 1.25%. We did not use  $^{61}\text{Ni}$  enriched compound to measure this hyperfine interaction. However, the metal nuclear hyperfine interactions in the palladium complexes and the large deviation of the  $g_{\text{av}}$  values from the free electron value indicate that in these cases the unpaired electron is at least partially localized in the orbitals of the metal. For nickel complexes, though no direct proof using hyperfine interaction can be furnished, the large deviation of the  $g_{\text{av}}$  values from that of free electron is suggestive enough to say that, here also the unpaired electron is at least partially localized in the orbitals of the metal.

The Table 4.3.1 also gives the esr parameters of some of the similar complexes for comparison. It is interesting to note here that by normal coordinate analysis and using extended Hückel MO calculations Schlöpfer and Nakamoto [205] have calculated the electron density of metal character in the highest occupied molecular orbital. Their analysis placed  $\text{S}_2\text{C}_2(\text{CN})_2^{2-}$  coordinated nickel complex as having 38% of electron density of metal d character in the HOMO. A detailed calculation based on esr studies of a number of dicyanodithiolene complexes by Holm and coworkers [207] suggested a different ground state for  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{2-}$  as,

$(AsPh_4) [Ni(S_2C_2(COPh)_2)_2]$   
in powder form



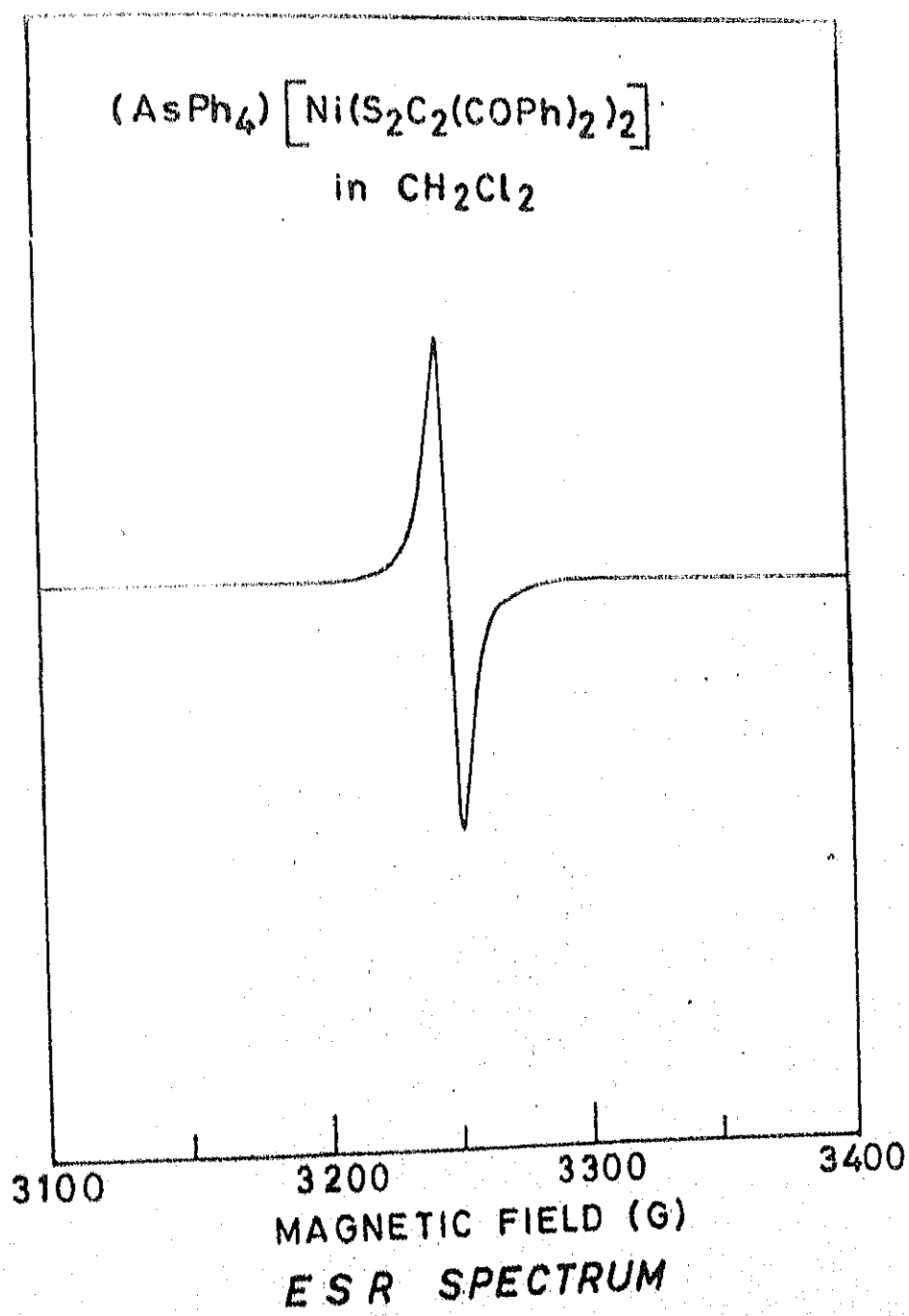
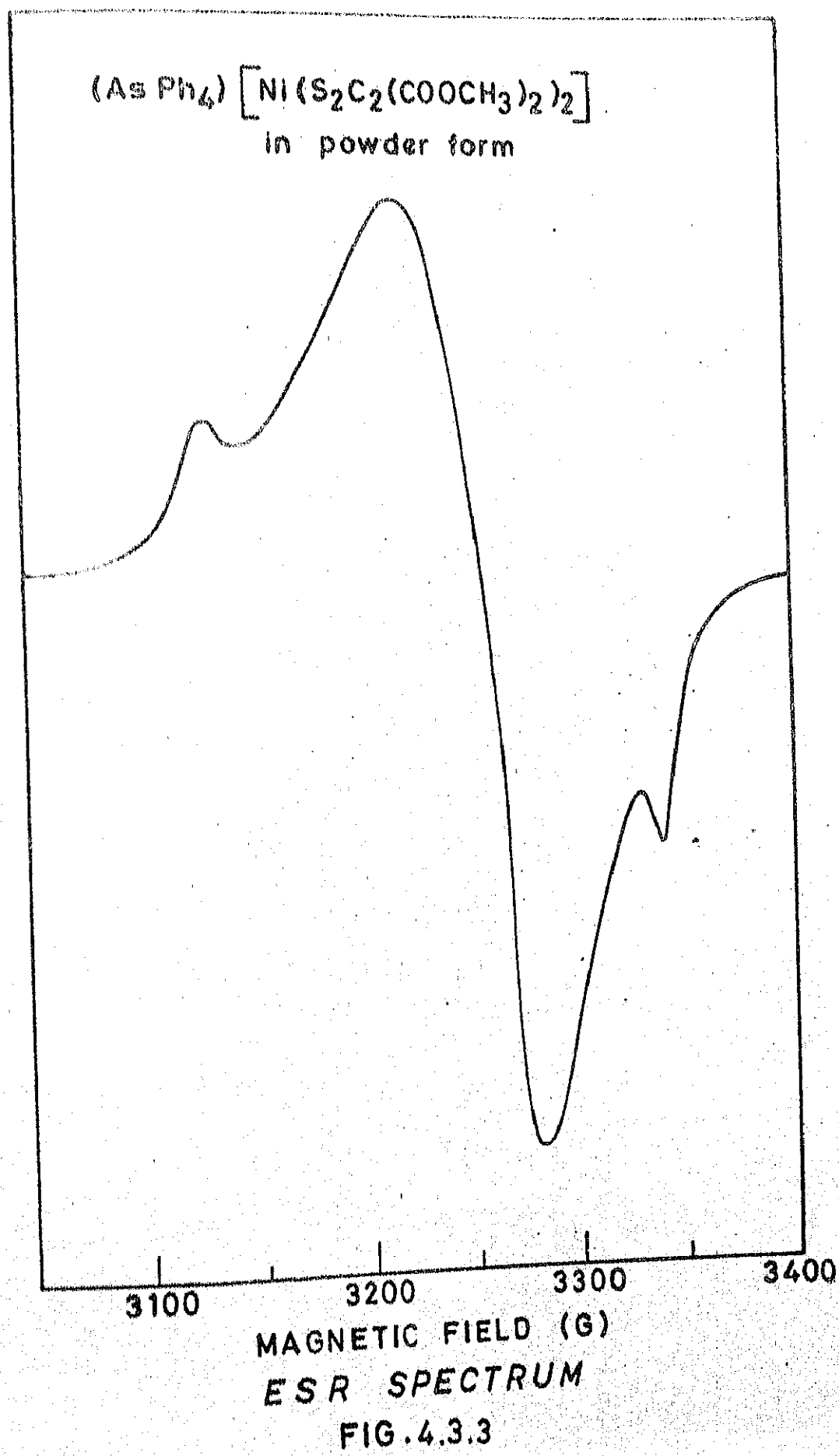
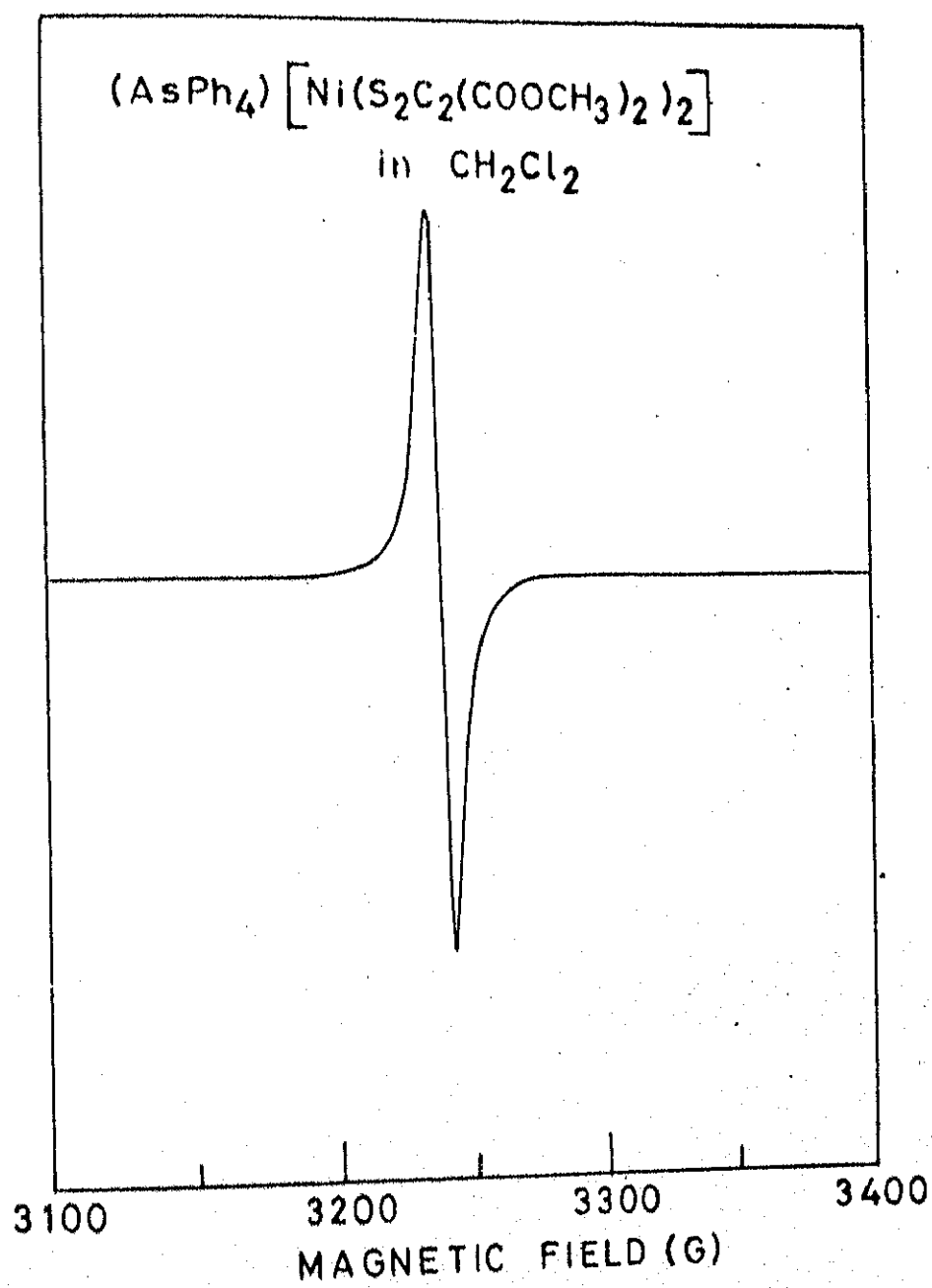


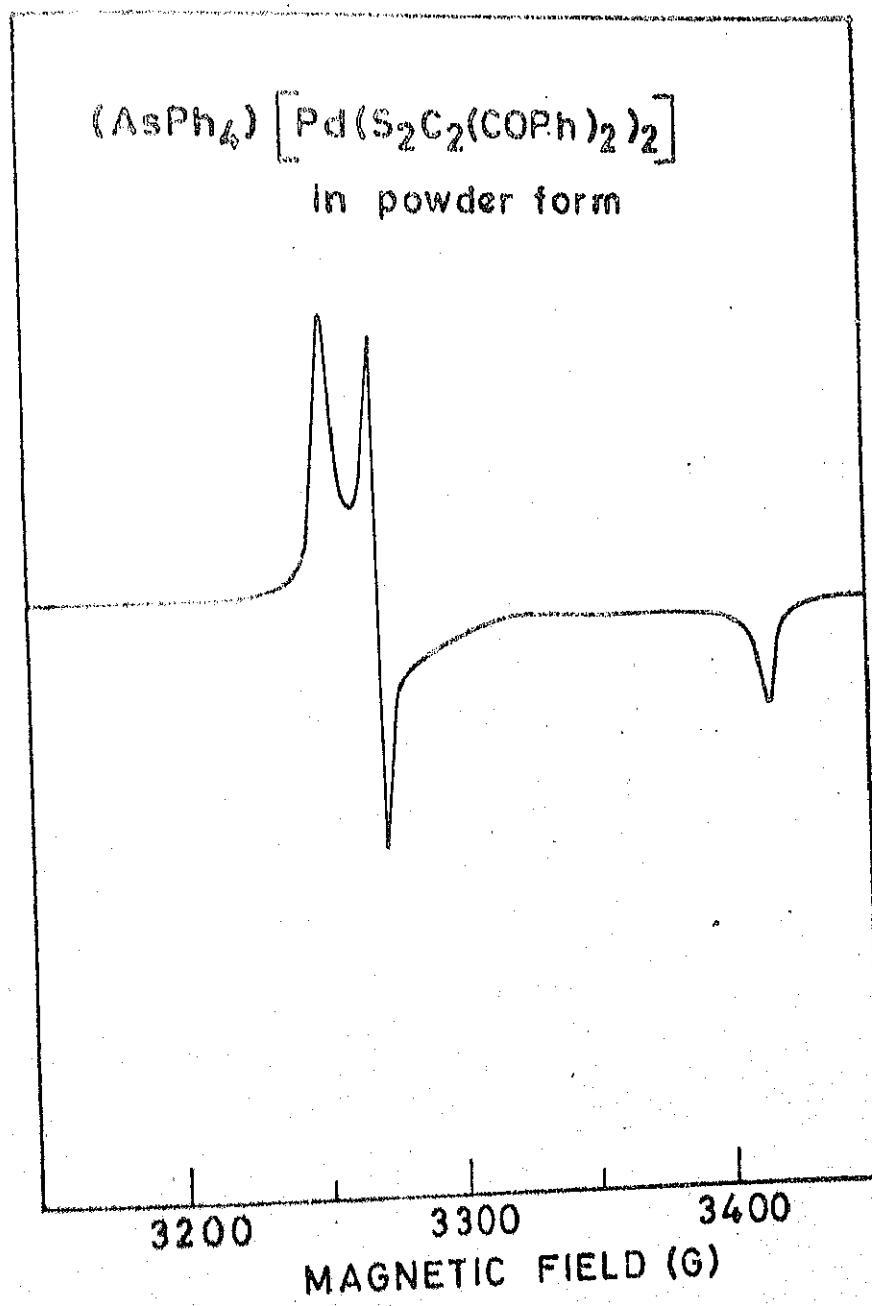
FIG. 4.3.2





ESR SPECTRUM

FIG. 4.3.4



ESR SPECTRUM

FIG. 4.3.5



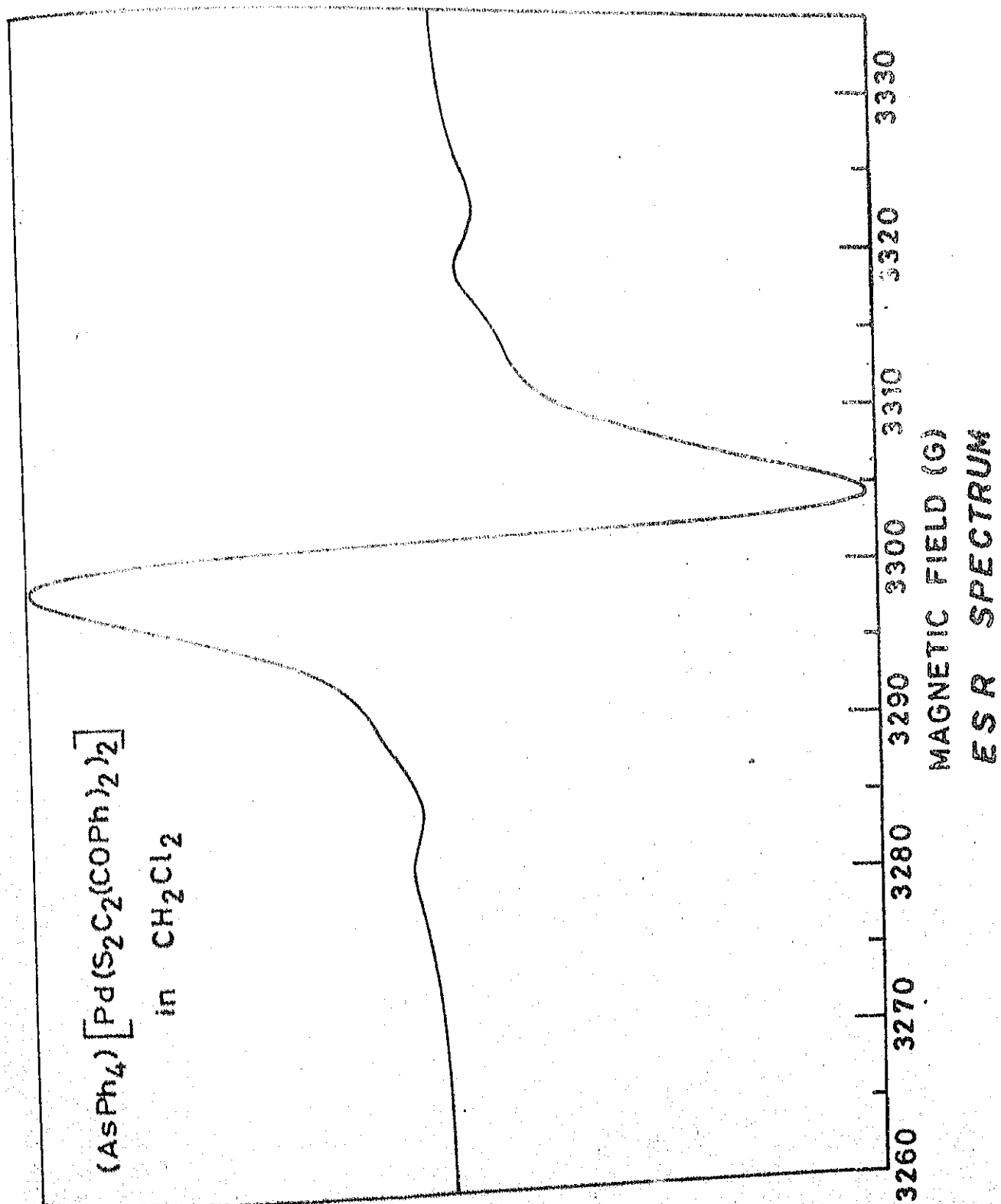


FIG. 4.3.6



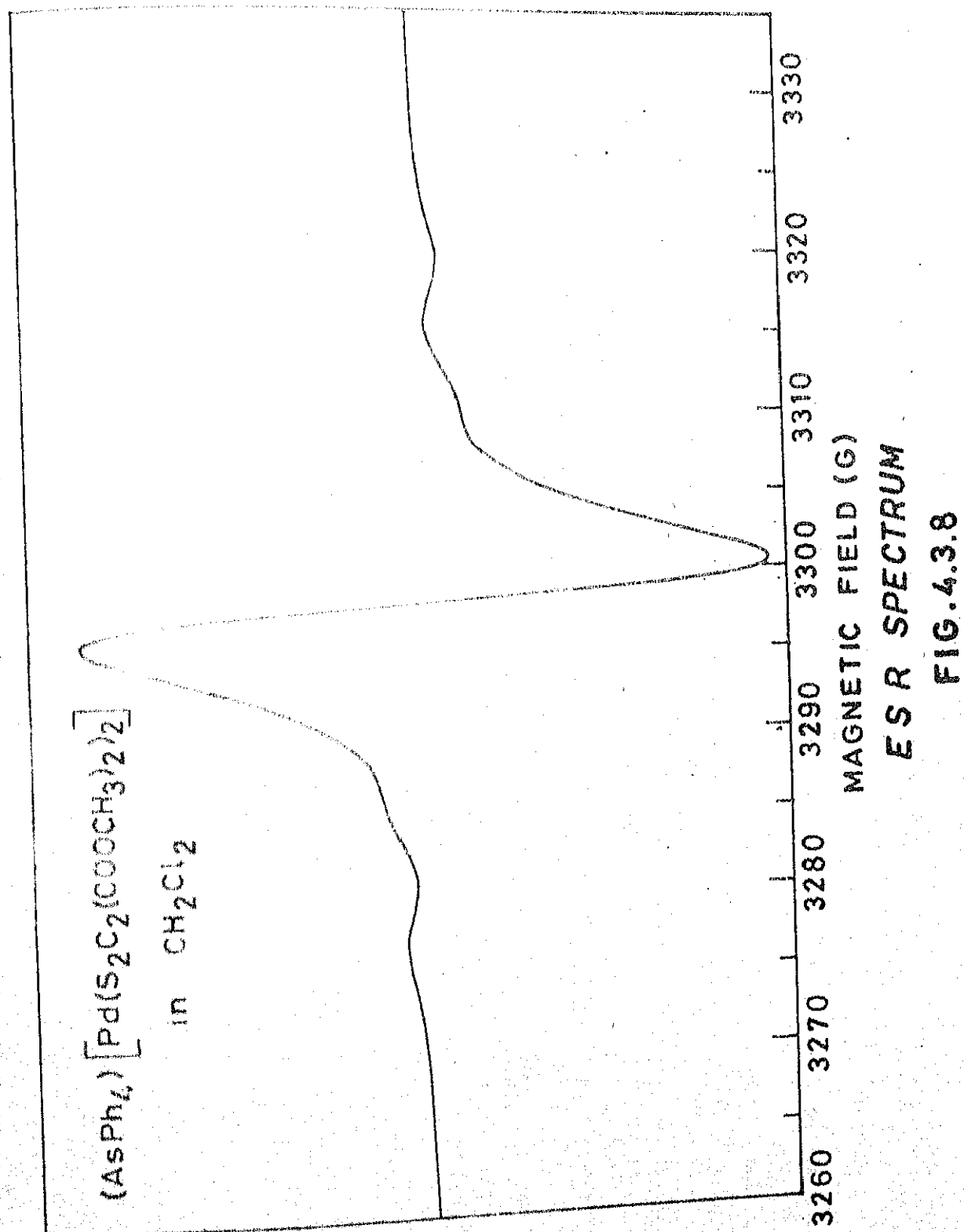


Table 4.3.1 Magnetic susceptibility and esr spectral data for the mononegative dithiolene complexes

Complex	$\mu_{\text{eff}}$ B.M.	$\tau_1$	$\tau_2$	$\tau_3$	$\langle \tau \rangle$	$\lambda_{\text{iso}}$ G	% Metal Character of the HOMO	Reference
1	2	3	4	5	6	7	8	9
$[\text{Ni}(\text{S}_2\text{C}_2(\text{CO}_2\text{H})_2)_2]^-$	1.79	2.143	2.055	2.011	2.0702	-	-	This work
$[\text{Ni}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^-$	1.80	2.148	2.064	2.013	2.0725	-	-	This work
$[\text{Pd}(\text{S}_2\text{C}_2(\text{CO}_2\text{H})_2)_2]^-$	1.76	2.069	2.057	1.970	2.0382	7.0	-	This work
$[\text{Pd}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^-$	1.77		2.034		2.0391	7.0	-	This work
$[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$	1.83	2.160	2.042	1.998	2.0630	-	$38^a(42)^b$	202, 205, 211
$[\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-$	1.85	2.137	2.044	1.996	2.0618	-	$43^a$	205, 211
$[\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]^-$	1.82	2.122	2.041	1.999	2.0568	-	$23^a$	205, 211
$[\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2]^-$	-	2.126	2.039	1.996	2.0560	-	$6^a(18)^c$	198, 205, 211

.....contd.

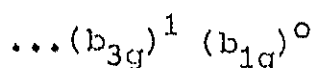
Table 4.3.1 (contd.)

1	2	3	4	5	6	7	8	9
$[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$	-	2.065	2.046	1.956	2.0238	7.7	-	211
$[\text{Pd}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-$	1.73	2.065	2.049	1.955	2.0230	7.7	-	211

a, Calculated by Hückel MO theory.

b, Estimated from esr spectral study.

c, Estimated from electronic spectral study.



and this half-filled orbital was calculated to be 42% metal in character. A progressive increase in the metal d character has been noticed for the series  $[\text{Ni}(\text{S}_4\text{C}_4\text{R}_4)]^-$  in the order  $\text{R} = \text{H} < \text{C}_6\text{H}_5 < \text{CF}_3 < \text{CN}$ . Interestingly the progressive increase in  $g_{av}$  values is also found for the same series (see Table 4.3.1). The isolated complexes in this study show the highest  $g_{av}$  values implying more nickel d character of the half-filled orbital in these cases. As the degree of participation of ligand or metal orbitals in the molecular orbital accommodating the unpaired electron would vary significantly depending on the substituent group, it is evident that similar situation should hold good for palladium system. The  $g_{av}$  values of the palladium complexes under present investigation show the same trend (see Table 4.3.1) suggesting also a similar situation. Thus, out of the two extreme formalisms, we have reasons to believe that these complexes can be regarded as square-planar containing  $\text{M(III)} (d^7)$  metal ion.

#### 4.4 X-Ray Photoelectron Spectral Study

The compound  $(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$  described in this thesis is novel because, here, the  $\text{S}_5^{2-}$  ligand is coordinated to nickel to form a six membered  $\text{M-S}_5$  ring whereas in other compounds containing nickel(II) and palladium(II) it is the  $\text{S}_4^{2-}$  which is coordinated to the metal forming a five membered ring. X-ray

photoelectron spectroscopy can help to study the binding energies of the atoms in this compound. Furthermore, this technique can also be used to estimate the charge distribution on the various atoms of the compound. The charge distribution in  $[\text{Ni}(\text{CN})_4]^{2-}$ , which is the starting material for our compound, has been estimated using this technique and the values obtained are found to be in good agreement with the theoretical values calculated using the SCF-MO method [212]. When applying this technique for the evaluation of charge distribution in coordination compounds, it is necessary to have careful calibration for compensating surface charging effects. Larsson and Folkesson [213,214] have used the  $\text{C}_{1s}$  binding energy of a phenyl group present in the molecule in the form of tetraphenylphosphonium ion as the internal standard. The chemical state of this phenyl group has been characterized by measuring the infrared absorption intensity of the C-H stretching vibrations. The relation between this intensity and the  $\text{C}_{1s}$  binding energy is then used to determine that value of the  $\text{C}_{1s}$  binding energy which has to be used as a reference. In this way Folkesson and coworkers [214-218] have been able to get a linear relationship between the appropriate core level binding energies and the atomic charge for a series of elements. Thus, the principle of the use of internal standards for the calibration of the spectra of the solid samples has been established.

The other principle of the XPS is the postulate that if such standards are used, it is possible to apply the very simple

relation

$$E_b = kq_{\text{eff}} + E_{bo} \quad \dots (1)$$

where  $q_{\text{eff}}$  is the effective charge of the atom under consideration,  $E_b$  is the observed binding energy and  $E_{bo}$  is a constant characteristic of the element.

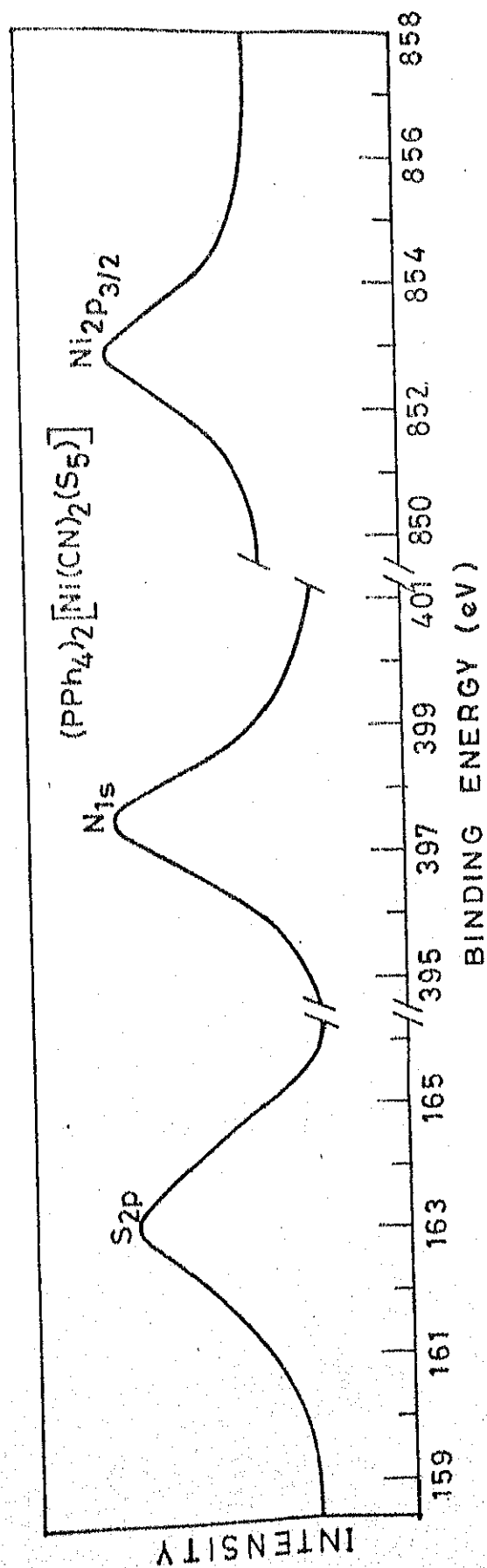
In many cases this simple approach has given good adherence to Eqn. (1) for a series of small molecules or ions where the charge of the atom under investigation could be 'taken' from independent, quantum chemical calculations. The validity of this relationship has also been tested by investigating a series of coordination compounds including our starting material  $[\text{Ni}(\text{CN})_4]^{2-}$  [212]. One prerequisite for a successful result in determining the charge distribution in complexes of the type  $[\text{M}(\text{L})_n]^{m-}$ , is that the number 'm' in the formula should be an exact integer. This means that we must use as a counter ion, a big, completely nonpolar, nonreactive ion so that no charge transfer or hydrogen bond effects can appear. We have used the tetraphenylphosphonium ion as the counter cation which satisfies all these criteria.

The spectrum of  $(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$  is reproduced in Fig. 4.4.1. The  $\text{S}_{2p}$  peak shows a broad structure as the compound has different types of sulfur atoms. If one considers that two sulfur atoms are similar (the ones bound to the metal) and different from the other three sulfur atoms, then, it is



possible to make a deconvolution procedure according to Siegbahn *et al.* [219]. As  $S_{2p}$  peak is comprised of different forms of sulfur one must compare the half-width (FWHM) of the  $S_{2p}$  peak measured with the halfwidth of a single  $S_{2p}$  peak. The half-width of a  $S_{2p}$  peak in sulfur ligands (e.g.,  $S_2C_2(CN)_2^{2-}$ ) is 2.7 eV. Then it is possible to resolve the broad  $S_{2p}$  peak into two different peaks with intensity ratio 2:3. The  $S_{2p}$  binding energy for coordinated  $S_5^{2-}$  group, thus, could be resolved into 162.8 eV (2S) and 163.6 eV (3S), respectively. The sulfur atoms bonded to metal have lower value compared to the other three sulfur atoms. This is obvious since the sulfur atoms bound to the metal are more negatively charged than the other three sulfur atoms. The observed binding energies are listed in Table 4.4.1.

Using the established relations for  $S_{2p}$ ,  $N_{1s}$  and  $Ni_{2p_{3/2}}$  [212,215,216] the charge distribution of all the atoms in this molecule are calculated and the values are tabulated in Table 4.4.2 along with the reported values for  $[Ni(CN)_4]^{2-}$ . From these results it is evident that the  $q_c$  is higher in this dicyano(pentasulfido)nickel(II) complex compared to the  $q_c$  of the starting tetracyanonickelate(II). This must be due to more backbonding from nickel to cyanide in the pentasulfido complex which corroborates the infrared results for this complex (*vide supra*).



X-RAY PHOTOELECTRON SPECTRUM

FIG.4.4.1

Table 4.4.1 Binding energies for  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ 

Compound	$E_b$ (eV)				Ref.
	$\text{S}_{2p}$	$\text{N}_{1s}$	$\text{Ni}_{2p_{3/2}}$	$\text{P}_{2p}$	
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$	162.8 (2S) 163.6 (3S)	397.6	852.9	133.7	This work
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_4]$	-	398.0	855.3	133.6	212

Table 4.4.2 Estimated charge distribution in  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  a

Compound					Ref.
	$q_S$	$q_N$	$q_{\text{Ni}}$	$q_C$	
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_2(\text{S}_5)]$	-0.30 (2S) -0.06 (3S)	-0.54	+0.68	-0.41	This work
$(\text{PPh}_4)_2[\text{Ni}(\text{CN})_4]^b$	-	-0.41 (-0.46)	+1.10 (+0.81)	-0.29 (-0.24)	212 220

a, The charges on sulfur ( $q_S$ ), nitrogen ( $q_N$ ) and nickel ( $q_{\text{Ni}}$ ) are calculated using the following relationships [212,216]:

$$E_b(\text{S}_{2p}) = 3.38 q_S + 163.8$$

$$E_b(\text{N}_{1s}) = 7.00 q_N + 401.4$$

$$E_b(\text{Ni}_{2p_{3/2}}) = 6.74 q_{\text{Ni}} + 848.3$$

Charge on carbon ( $q_C$ ) could be calculated since the total charge of the ion ( $-2$ ) is known.

b, Values obtained by SCF MO method are given in parenthesis.

#### 4.5 Electrochemical Studies

The electrochemical oxidation and reduction properties of  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  and  $[\text{Ni}(\text{CS}_4)_2]^{2-}$  are studied using cyclic voltammetry (CV) and differential pulse polarography (DPP). The measurements were done in DMF using tetrabutylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte. DPP measurements were performed with a 25 mV pulse amplitude so that derivative pulse mode relationships [221] valid for small pulse amplitudes apply. The cyclic voltammograms and differential pulse polarograms are reproduced in Figs. 4.5.1 and 4.5.2. The observed redox potentials are listed in Table 4.5.1.

As  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  is unstable in solution we could not do much with this system. It undergoes irreversible reduction  $[-1.825 \text{ V (CV); } -1.755 \text{ V (DPP)}]$  and while this process is on, the reduced species, deposits on the platinum electrode surface, making the electrode not useful for further investigation. For this compound CV could not be recorded above +0.7 V as the compound decomposes and deposits on the electrode surface.

For  $[\text{Ni}(\text{CS}_4)_2]^{2-}$ , a quasireversible oxidation and irreversible reduction processes can be seen. However, in the electrochemical studies both in the anodic as well as in the cathodic scan spurious peaks appear at different positions, respectively, suggesting decomposition of the complex during the redox process. Cyclic polarogram study of this complex has been reported by Coucouvanis and Fackler [179], however, only the oxidation

potential value for the system is given. In our DPP study we observed two peaks during the oxidation process, the second wave at higher positive potential is poorly developed and whose diffusion current is very low. The halfwidths of the DPP peaks are listed in Table 4.5.1. From the cyclic voltammogram, however, only the second potential can be observed. The differential pulse polarogram clearly suggests two different oxidation stages at +0.305 V and +0.445 V, respectively. Hence, it is apparent from this study that it is easy to oxidize  $[\text{Ni}(\text{CS}_4)_2]^{2-}$  to the corresponding mononegative and even to the neutral complex. Halfwidths of the DPP peaks of this quasireversible process and of  $[\text{Ni}(\text{CN})_2(\text{S}_5)]^{2-}$  species suggest an one electron change in these redox reactions [221].

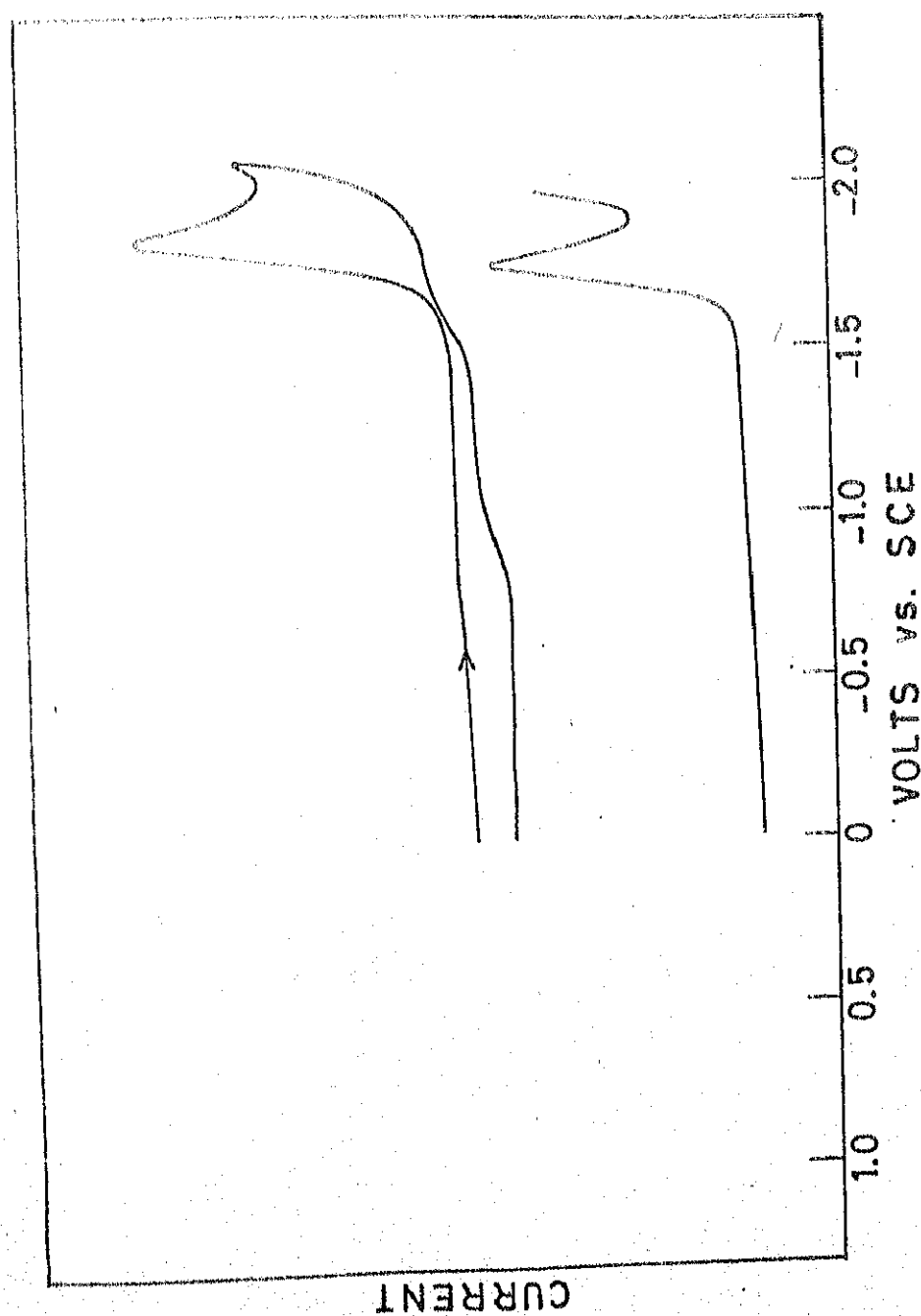


FIG. 4.5.1 CYCLIC VOLTAMMOGRAM AND DIFFERENTIAL PULSE  
POLAROGRAPH FOR  $(PPH_4)_2[Ni(CN)_2(S_5)]$   
SCAN RATE 100  $mVs^{-1}$  (CV) 5  $mVs^{-1}$  (DPP)

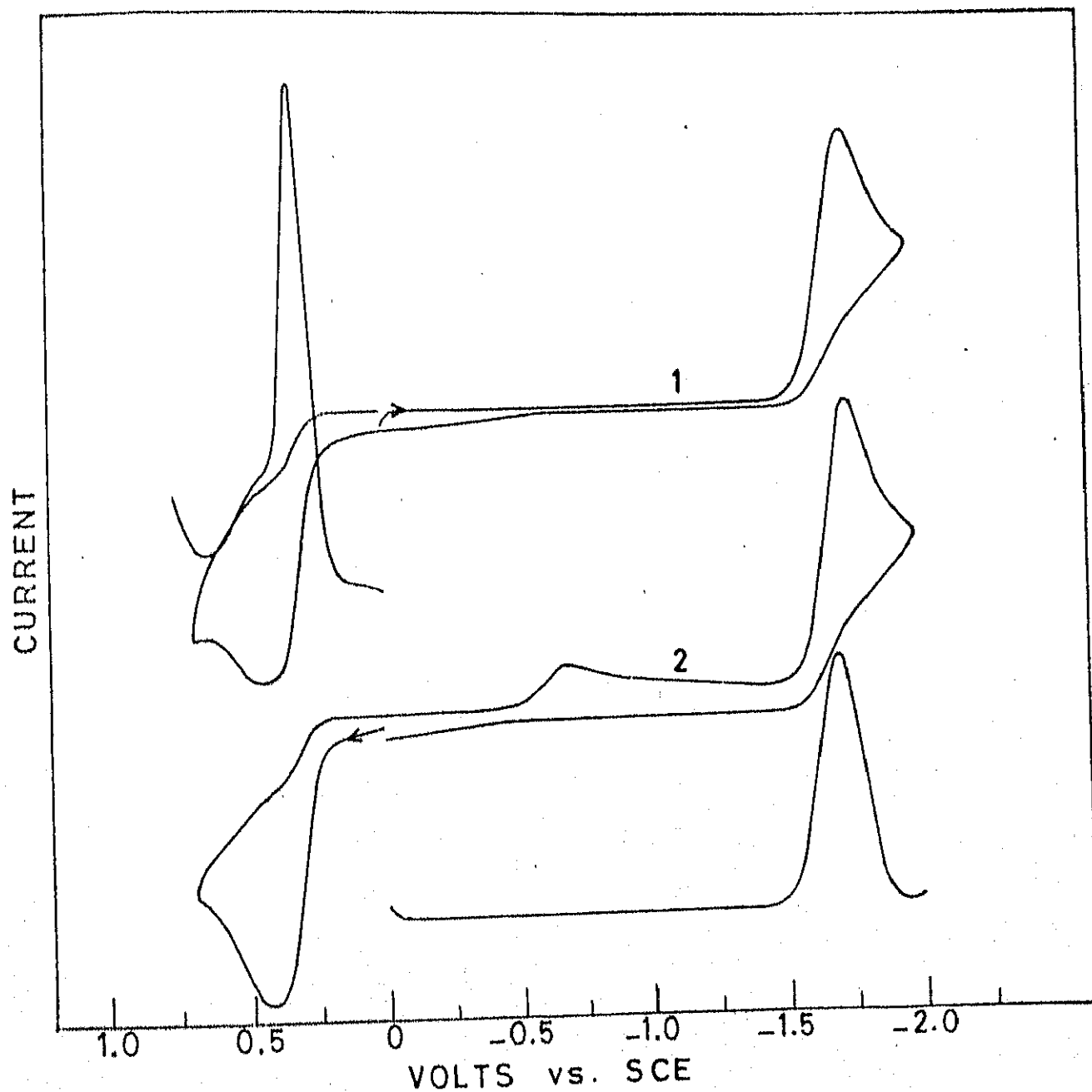


FIG.4.5.2 CYCLIC VOLTAMMOGRAM AND DIFFERENTIAL PULSE POLAROGRAM FOR  $(\text{AsPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$

1. CATHODIC SCAN 2. ANODIC SCAN  
SCAN RATE  $100 \text{ mVs}^{-1}$  (CV)  $2 \text{ mVs}^{-1}$  (DPP)

Table 4.5.1 Electrochemical Redox Potentials (vs SCE)<sup>a</sup>

Complex	(E <sub>p</sub> ) <sub>A</sub> (V)	(E <sub>p</sub> ) <sub>C</sub> (V)	E <sub>p</sub> (V)	DPP peak halfwidth (mV)
[Ni(CN) <sub>2</sub> (S <sub>5</sub> )] <sup>2-</sup>	-	-1.825	-1.755	120
[Ni(CS <sub>4</sub> ) <sub>2</sub> ] <sup>2-</sup>	+0.44	-1.750	-1.790	195
			+0.305	105
			+0.445	-

<sup>a</sup> (E<sub>p</sub>)<sub>A</sub> = Anodic potential (CV)

(E<sub>p</sub>)<sub>C</sub> = Cathodic potential (CV)

E<sub>p</sub> = Differential pulse polarographic potential.



## CONCLUSIONS

### AND SCOPE FOR FUTURE WORK

From the foregoing discussion it is apparent that polysulfides as ligands have a fascinating chemistry. The stability of the polysulfido complexes in nickel family increases down the group. For nickel and palladium in their normal oxidation state of +2, the coordinated polysulfide is usually  $S_4^{2-}$ . However, in the case of palladium the polymeric  $[PdS_{11}]^{2-}$  is also formed. In the case of platinum, it is known that bispentasulfido complex is formed even in the +2 oxidation state [56]. When the oxidation state of the metal is +4, tris-pentasulfido complexes are formed in the case of palladium and platinum. Curiously the oxidizing agent here is the polysulfide ion. In the case of nickel, however, polysulfide could not oxidize Ni(II) to Ni(IV), probably because the potential required to oxidize Ni(II) to Ni(IV) is much higher and polysulfide may not provide such high oxidizing environment.

In the case of substituted polysulfide complexes, the chemistry of nickel and palladium are alike, when the coligands used are aromatic diimines. Again the polysulfide coordinated here is  $S_4^{2-}$ . It is known that when the coligands used are phosphines, palladium and platinum have similar chemistry [40].

The nickel complexes are interesting because the polysulfide ligands could stabilize the nickel system in square-planar geometry. Another interesting aspect of polysulfide coordinated nickel complexes is their reactivity. Coordinated tetrasulfide in nickel is attacked by oxygen leading thereby to the formation of coordinated  $S_3O_2^{2-}$  which might be relevant to the oxidation of  $S^{2-}/S^0$  systems using metal complexes as catalysts in biosphere.

Another interesting complex isolated is the  $[Ni(CN)_2S_5]^{2-}$  which contains a pentasulfido ligand. The increased size of the polysulfide chain may be due to the presence of cyanide as coligands. Hence it would be interesting to study the effect of coligands on the polysulfide chain length. Since the instability of this compound prevented us from doing any solution studies, an approach was made to understand the charge distribution by the use of XPS. This type of studies have been conducted in some other systems [212] and the results are found to be in good agreement with the theoretical results obtained by quantum chemical calculations. This method has the potential to estimate the charge distribution in complex molecules, where, the quantum mechanical calculations may be difficult.

The reactivity of the polysulfido complexes may be dictated by the ring strain present in  $MS_4$  and  $MS_5$  type of complexes. Thus, to achieve planarity of the ring whereby delocalization of the  $\pi$ -electron density could be achieved, the complexes undergo smooth reaction with  $CS_2$ , COS and substituted acetylenes at ambient temperature. The stability of these newly formed hetero ring systems depend on the extent of  $\pi$ -bonding. For  $CS_2$  it is evident that the stereochemistry along with the number of d-electrons present in the system dictates the reaction. Thus, in the normal oxidation state of nickel and palladium (+2) the coordinated  $S_4^{2-}$  readily reacts with  $CS_2$  forming  $CS_4^{2-}$ . However, for the hexacoordinated species containing palladium or platinum in the +4 oxidation state this reaction does not proceed. However, similar reactions with substituted acetylenes give the corresponding dithiolenes irrespective of the oxidation state of the metal atom and the coordination number. Interestingly, the nickel(II) and palladium(II) tetrasulfido complexes on reaction with acetylenes give the dithiolene complexes with a concomitant oxidation of the starting dianion to monoanion. The reactions of nickel system are of special interest in this regard since the resting hydrogenase enzyme containing nickel is in the +3 oxidation state. The dithiolene systems generated here show appreciable metal character of the highest occupied molecular orbital accommodating the odd electron, thus, suggesting a formal +3 oxidation state for the metal atom. The nickel(III) systems

are rare and they are not stable under normal conditions. These dithiolene systems are stable at normal conditions and can be readily oxidized to the corresponding tetravalent state, but by mere solvent interaction they revert back to the trivalent state. The esr signals of the nickel containing hydrogenases are similar to the ones reported here, but show greater anisotropy and higher  $\langle g \rangle$  values. Nonetheless it would be a good scope for the future work to react these polysulfide complexes with different activated acetylenes to have  $\langle g \rangle$  values similar to the native nickel hydrogenase system and to simulate the hydrogenase activity in vitro.

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